GEORGIA INSTITUTE OF TECHNOLOGY
STATE ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

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REPORTS

PROJECT NO. 228-197

STANDARDIZATION OF SURFACE PROPERTIES OF FINE PARTICLES

BY

J. M. DALLAVALLE, CLYDE ORR, JR.
H. G. BLOCKER AND J. B. GARRETT

CONTRACT NO. DA-36-039-SC-42588

DEPARTMENT OF THE ARMY PROJECT: 3-99-15-022
SIGNAL CORPS PROJECT: 152B

JULY 30, 1953-APRIL 30, 1954

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ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

QUARTERLY REPORT NO. 1

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I. ABSTRACT

This investigation has as its general objective an evaluation of the surface properties of finely divided solids such that the standardization of these properties may eventually be attained, and it has as its immediate objective a study of the heat released upon the adsorption of a gas by powders.

A suitable instrument has been devised for making these heat of adsorption measurements, and a number of measurements have been made. All indicate that the heat liberated upon the adsorption of a unit quantity of gas varies as the surface of the solid absorbent is covered. Surprisingly, the first small increment of gas adsorbed by cocoanut charcoal gives up a quantity of heat that seems to be approximately equal to the heat of liquefaction of the gas at that temperature, while later increments of adsorbing gas give up considerably greater increments of heat until the surface is covered with a monomolecular layer, at which conditions only heat equivalent to liquefaction is released.

Efforts in the immediate future will be directed toward making more measurements to confirm these trends.

II. PURPOSE

This investigation, relating both to the fields of solid-state chemistry and to fine-particle technology, has as its general objective an evaluation of the surface properties of finely divided solid materials such that the standardization of these properties may eventually be attained. The heat of adsorption, i.e., the heat liberated when a gas is adsorbed on the surface of a powdered solid, is currently the property of primary interest, while the catalytic activity of the powder, its specific

surface area and the relation of these to the powder's heat of adsorption characteristics are of secondary interest.

Only heat of adsorption has been studied during this report period, although in some cases specific surface area measurements have been made in conjunction with those of heat of adsorption. The work has consisted of three primary parts: (1) calorimeter construction and design, (2) thermodynamic calculations pertaining to liquid nitrogen and liquid oxygen mixtures and (3) heat of adsorption measurements. These are discussed in the following sections.

III. EXPERIMENTAL WORK

A. Calorimeter Construction

The heat of adsorption apparatus built for similar work on a previous contract was described, and a schematic diagram of it was presented in the final report[1] of that work. To accomplish improved operation, several changes were made in the apparatus at the beginning of this investigation. First, the calorimeter proper, including the sample tube, the evaporation chamber and Dewar flasks, was rebuilt so that the volume of the sample tube was about four times larger than previously. This was done so that larger samples, producing greater quantities of heat, could be employed in order to increase the accuracy of the measurements and, at the same time, to permit smaller increments of heat to be detected. Second, the sample tube was made of Vycor, a glass capable of withstanding higher temperatures than Pyrex glass. This permitted the sample whose heat of

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1 DallaValle, J. M., Orr, C., Jr., and Blocker, H. G., Research on Surface Properties of Fine Particles. Final Report, Project 181-119, Contract No. DA-36-039-sc-5411, Georgia Institute of Technology, Atlanta, April 30, 1953.

adsorption was to be measured to be heated to a higher temperature, and, hence to be freed more rapidly of previously adsorbed gases. Third, the thickness of the wall of the sample tube was reduced by controlled etching with hydrofluoric acid to a thickness of about 0.2 mm. Etching was limited to the outside of the sample tube so that a smooth surface could be maintained on the inside where adsorption must occur. The thin wall was desirable because it permitted rapid heat transfer between the sample and the calorimetric medium (liquid nitrogen) surrounding the sample tube and also reduced heat transfer along the wall in a direction lateral to the desired direction of heat flow. Finally, a two-stage, fractionating diffusion pump and a mechanical forepump with greater capacity were added to the evacuating system to speed sample preparation.

B. Thermodynamic Calculations

Liquid nitrogen was employed as the calorimetric medium while most of the previous measurements were being made and will continue to be employed in the future. Since commercial liquid nitrogen usually contains some liquid oxygen, it was deemed necessary to establish pertinent thermodynamic relationships for this mixture over the required range. Only limited heat of vaporization data could be found in the region of interest; hence, it was necessary to calculate the required information from other thermodynamic properties using such data as were available.

Assumptions had to be made in order to carry out the calculations. These assumptions may be listed as (1) a mixture of liquid nitrogen and liquid oxygen is an ideal solution, (2) the vapor phase is a mixture of ideal gases, (3) the vapor and liquid phases are in equilibrium, (4) the specific volume of the vapor phase is described by generalized

compressibility factors and (5) the change in specific volume because of evaporation of either liquid nitrogen or oxygen is proportional to the specific volume of the vapor. It will be seen from the results presented at the close of this section that these assumptions, when the range of variation is taken into account, are quite acceptable.

Calculations were based on the Clapeyron-Clausius equation by which, at a given temperature, the heats of vaporization of nitrogen and oxygen may be written

$$\Delta H_n = T\Delta V_n \left(\frac{dp}{dT}\right)_n \qquad (1)$$

and

$$\Delta H_o = T\Delta V_o \left(\frac{dp}{dT}\right)_o \qquad (2)$$

when the subscripts n and o refer to nitrogen and oxygen, respectively, ΔH is the heat of vaporization, ΔV is the change in volume due to evaporation, p is the pressure and T is the absolute temperature. The quantity dp/dT was determined for nitrogen and oxygen from the vapor pressure-temperature relationships given by Farkas and Melville[2] which are, respectively,

$$\log p_n = -\frac{334.64}{T} + 7.5778 - 0.00476T \qquad (3)$$

and

$$\log p_o = -\frac{419.30}{T} + 8.1173 - 0.00648T \qquad (4)$$

if pressures are expressed in millimeters of mercury and temperatures in degrees Kelvin. The specific volumes of the vapor phases were obtained from the equations

$$V_n = \frac{ZRT}{p_n} \qquad (5)$$

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2 Farkas, A., and Melville, H. W., Experimental Methods in Gas Reactions. McMillan and Company, Ltd., London, 1939.

and

$$V_o = \frac{ZRT}{p_o} \tag{6}$$

where Z is a generalized compressibility factor such as may be evaluated from charts given by Hougen and Watson[3] and R is the gas constant.

As a consequence of the assumptions listed above, if ΔH is the heat of vaporization of liquid nitrogen and oxygen mixtures, if y_n and y_o are the mole fractions of nitrogen and oxygen, respectively, in the vapor phase, if x_n and x_o are the mole fractions of the nitrogen and oxygen, respectively, in the liquid phase and if p is the total pressure, it may be written that

$$p = x_n p_n + x_o p_o \ , \tag{7}$$

$$x_n + x_o = 1 \ , \tag{8}$$

$$y_n p = x_n p_n \ , \tag{9}$$

$$y_o p = x_o p_o \ , \tag{10}$$

and

$$\Delta H = y_n \Delta H_n + y_o \Delta H_o . \tag{11}$$

Over the temperature range from 76° to 90° K., values of p_n, p_o, ΔH_n, ΔH_o and ΔH were calculated using the appropriate equations and combinations of equations presented above. The heat of vaporization of the mixture was calculated for a pressure of 740 mm. Hg, the mean atmospheric pressure for this locality. The results are given in Table I.

Temperatures for the commercial liquid nitrogen used in this investigation have been observed to vary between 77.6° and 80.0° K. and to change no more than 0.1° K. in eight hours.

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3 Hougen, O. A., and Watson, K. M., Chemical Process Principles Charts. John Wiley and Sons, Inc., New York, 1947.

TABLE I

VAPOR PRESSURE AND HEAT OF VAPORIZATION OF OXYGEN, NITROGEN AND THEIR MIXTURES

Temp. (°K.)	Nitrogen in Liquid Bath (Per Cent)	Vapor Pressure of O_2 (mm. Hg)	Vapor Pressure of N_2 (mm. Hg)	Heat of Vaporization of O_2 (Cal./Mole)	Heat of Vaporization of N_2 (Cal./Mole)	Heat of Vaporization of N_2-O_2 Mixture at 740 mm. Hg (Cal./Mole)
76	100.0	128.1	650	1,788	1,346	1,346
77	100.0	148.9	734	1,779	1,338	1,338
78	97.0	172.3	825	1,770	1,330	1,343
79	93.2	198.5	924	1,761	1,320	1,350
80	88.8	227.9	1,032	1,752	1,312	1,362
81	83.8	260.6	1,150	1,743	1,304	1,376
82	78.0	296.8	1,278	1,733	1,295	1,391
84	64.1	381.3	1,564	1,712	1,276	1,432
86	46.6	483.5	1,893	1,689	1,257	1,487
88	24.7	605.8	2,271	1,661	1,233	1,555
90	0.0	750.2	2,699	1,632	1,210	1,632

C. Heat of Adsorption Measurements

Adsorption measurements with four different samples have been undertaken during the period covered by this report. One measurement attempt with a specially prepared nickel sample resulted in very doubtful values because the total surface area of the sample was not great enough to liberate an accurately measurable quantity of heat; it will not be discussed further here.

One measurement was made on a high-surface-area nickel-silica catalyst supplied by the Girdler Corporation, Louisville, Kentucky, and designated G-12. This material was originally prepared in the form of pellets having approximately one-quarter-inch diameters, but to increase its rate of adsorption the pellets were crushed and the fraction of this crushed product passing a 12-mesh screen but retained on a 20-mesh screen

was employed for the measurements. The specific surface area of this catalyst was not obtained because measurements were not continued to a sufficiently high pressure for a monolayer of adsorbed gas molecules to form.

Two measurements were made on the coconut charcoal sample, the preparation of which has been described elsewhere.[4] Heat of adsorption measurements have also been made and reported for this material, but each previous determination involved the heat liberated when a considerable portion of the adsorbent's surface was being covered, e.g., the increment from five to ten per cent coverage. These two latter measurements represent attempts to determine the heat liberated in increments equivalent to about 0.2 per cent coverage of the surface. These latter runs also were made with less highly degassed adsorbents. Only two points were obtained in the first of these two determinations because a tube leading from the calorimeter chamber became blocked with condensed water vapor from the atmosphere during the nighttime period when the run had to be interrupted. After steps were taken to prevent a reoccurence, the sample was re-evacuated and the latter of the two runs was made.

The results from these measurements are presented in Table II. It will be noted that both experimental and calculated data are included. With the exception of H_d, which now is used as the symbol for the measured incremental (approximately a differential) heat of adsorption, the symbols in the table are as defined in the final report[5] of the preceding project. Some of the charcoal results are also presented in Figure 1; the symbol H_L is used there to denote the heat of liquefaction of nitrogen.

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4 DallaValle, et al., op. cit.
5 DallaValle, et al., op. cit.

TABLE II

HEAT OF ADSORPTION DATA

Material	p_1 (mm. Hg)	p (mm. Hg)	V (cc./g.)	H_d $\left(\frac{\text{cal.}}{\text{g.}}\right)$	T_b (°K.)	T_g (°K.)	T_e (°K.)	Constants
Nickel-Silica Catalyst (evacuated 96 hrs. at 350° C. to 0.1 μ pressure)	75.0	0.0	0.43	0.109	300	79.4	285	W = 13.735 g. V_t = 65.2 cc. V_e = 3 cc. V_s = 57.2 cc.
	164.0	0.0	1.36	0.114	300	79.4	285	
	265.0	0.4	2.86	0.092	300	79.4	285	
	309.6	0.7	4.43	0.086	300	79.4	285	
	390.9	1.0	6.64	0.084	299	79.4	286	
	504.9	1.5	9.50	0.064	299	77.9	286	
	492.7	1.8	12.30	0.100	299	77.9	286	
	572.7	2.1	15.55	0.100	299	77.9	286	
	602.0	3.0	18.96	0.102	299	77.9	286	
Coconut Charcoal (evacuated 200 hrs. at 500° C. to 0.01 μ pressure)	38.2	0.0	0.35	0.186	302	77.8	288	W = 8.456 g. V_t = 65.2 cc. V_e = 3 cc. V_s = 68.8 cc. V_m = 338 cc./g.*
	41.9	0.0	0.73	0.123	302	77.8	288	
Coconut Charcoal (evacuated 24 hrs. at 500° C. to 0.07 μ pressure)	66.0	0.0	0.61	0.096	301	78.6	286	W = 8.456 g. V_t = 65.2 cc. V_e = 3 cc. V_s = 68.8 cc. V_m = 338 cc./g.*
	80.3	0.0	1.35	0.075	301	78.6	286	
	104.0	0.0	2.31	----	301	78.9	286	
	117.0	0.0	3.38	0.153	301	78.9	286	
	101.7	0.0	4.39	----	303	78.7	288	
	91.4	0.0	5.23	0.144	303	78.7	288	
	101.0	0.0	6.15	0.146	303	78.7	288	
	162.9	0.0	7.66	----	301	78.5	286	
	172.9	0.0	9.25	0.160	301	78.5	286	
	190.7	0.0	11.01	0.163	301	78.5	286	
	207.2	0.0	12.92	0.164	301	78.5	286	
	214.9	0.0	14.88	0.191	303	78.1	288	
	186.8	0.0	16.59	0.163	303	78.1	288	
	198.2	0.0	18.40	0.166	303	78.1	288	

*Obtained from run reported by DallaValle, et al., op. cit.

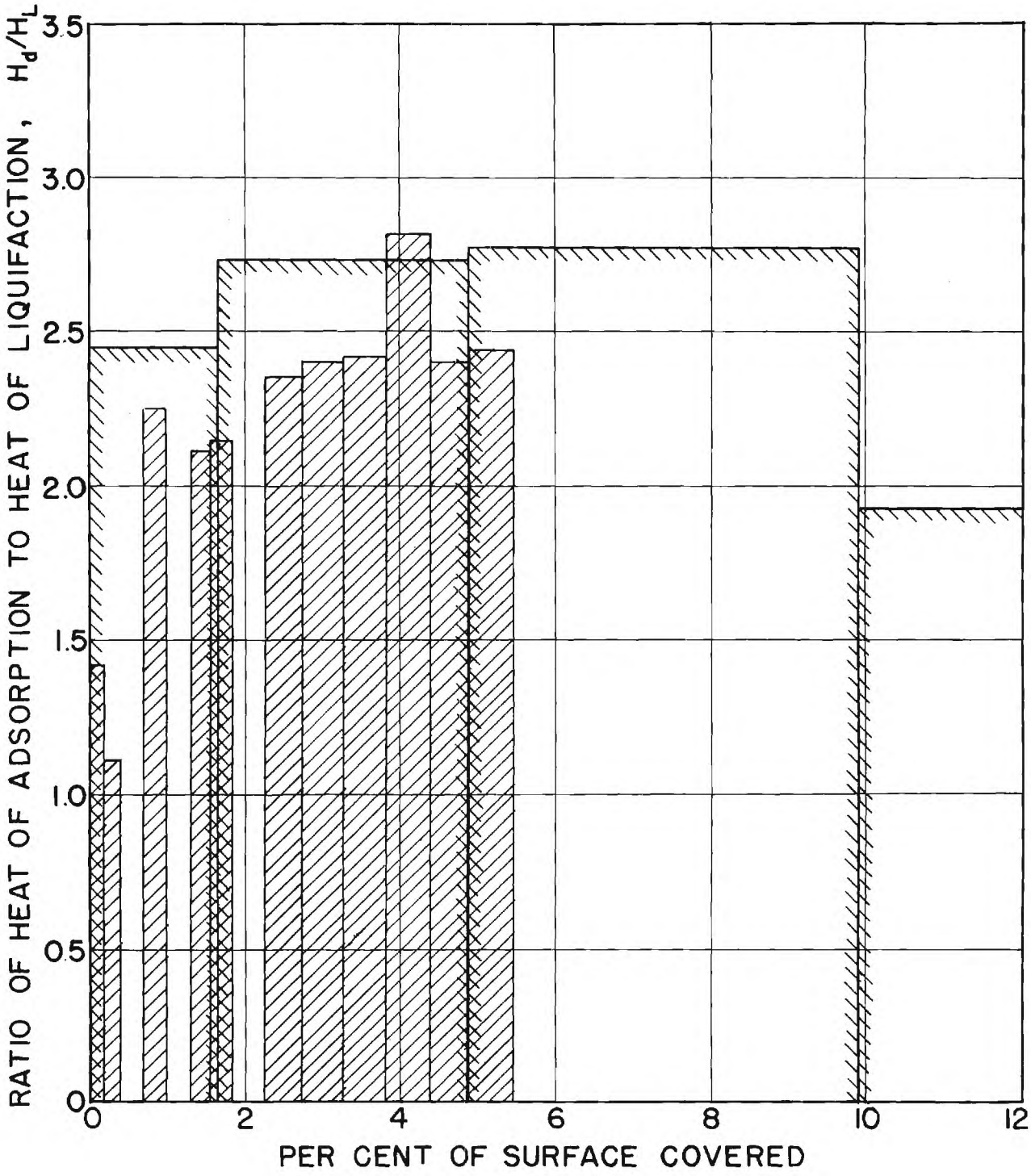

Figure 1. Heat of Adsorption as a Function of the Surface of Adsorbent Covered. (The Completely Crosshatched Areas Represent Data Obtained During this Report Period.)

IV. DISCUSSION OF RESULTS

The much smaller increments of heat which have been measured with the enlarged and rebuilt calorimeter show that this device has been greatly improved.

As Table I shows, the heat of vaporization of the liquid nitrogen and liquid oxygen mixtures likely to be encountered does not vary by more than about two per cent. By using the values in the table, however, the errors in heat of adsorption measurements due to variations in the calorimetric medium can be reduced to an insignificant figure.

The heat of adsorption results, with the exception of points at low coverage of the adsorbent, appear to be reasonably consistent and to follow the expected pattern. The fact that previously reported results for the coconut charcoal indicated somewhat higher heats of adsorption is probably due to differences in the degrees of degassing the samples. Some of the measurements indicate that the heat released by the first few adsorbed gas molecules is approximately the heat of liquefaction of the gas at that temperature.

V. FUTURE WORK

It is not planned to change the calorimeter until more results and experience have been obtained. Consequently, efforts will be directed toward making heat of adsorption measurements with several compounds. Because nickel is an important catalyst, and because experience has been gained in the past in its use, another attempt will be made to prepare a sample having a high specific surface area. If this can be done, not only will heat of adsorption measurements be attempted but a companion study of the catalytic activity of the material will be initiated.

As a means of reducing the long intervals of time required by heat of adsorption measurements, a separate gas adsorption apparatus will be built, and, as a means of heating samples to higher temperatures during degassing, an induction heater will be employed as soon as a line meeting the current requirements of the heater can be installed.

VI. PERSONNEL

The technical personnel who worked on this project and the percentage of working time each devoted to this project are shown below:

Name	Title	Percentage of Working Time During Entire Period Covered by Report
J. M. DallaValle	Project Director	10
Clyde Orr, Jr.	Research Engineer	50
H. G. Blocker	Research Engineer	100
R. A. Young	Research Physicist	2
W. E. Woolf	Research Physicist	5
Miss Jane Barrett	Research Assistant	18

Mr. Young and Mr. Woolf, x-ray specialists, made a preliminary study of the crystal structure of nickel by line-broadening methods.

Miss Barrett, a recent graduate of the Georgia State College for Women, joined the staff on July 1, 1953. She holds a B.S. degree in chemistry. In the future, she will devote about 50 per cent of her time to this project.

Respectfully submitted:

J. M. DallaValle,
Project Director

Clyde Orr, Jr.
Research Engineer

H. G. Blocker,
Research Engineer

Approved:

Herschel H. Cudd, Director
Engineering Experiment Station

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

QUARTERLY REPORT NO. 2

PROJECT NO. 228-197

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OCTOBER 30, 1953

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OCTOBER 30, 1953

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I. ABSTRACT

This investigation has as its general purpose an evaluation of the surface properties of finely divided solids; its immediate objective is a study of heat of adsorption, i.e., the heat released upon the adsorption of a gas by a solid.

Two completely different apparatus utilizing different principles were employed. Heat of adsorption measurements for the adsorption of nitrogen gas on charcoal at rather low temperatures indicated general agreement between the two methods. Heats of adsorption of nitrogen gas on a specially prepared nickel powder at low temperatures were also determined and are believed to be of the correct order of magnitude. A spreading of the experimental data, the source of which is not believed to be entirely experimental error, was evident, however. Additional work will be directed toward eliminating this source of error.

II. PURPOSE

The purpose of this investigation is an evaluation of the surface properties of finely divided solid materials so that the standardization of these properties may eventually be attained. In previous investigations under other contracts the evaluation of particle size and of specific surface area has been considered. The heat of adsorption, i.e., the heat liberated when a gas is adsorbed on the surface of a powdered solid, is the property of primary concern in this investigation.

An elucidation of the heat of adsorption phenomena is of great theoretical as well as practical importance, since the result is indicative of the energy states of atoms in surface layers. Much, then, is to be learned from heat of adsorption measurements about the structure of solid surfaces--why some

solids act as catalysts for particular reactions under certain conditions, about chemisorption, about physical adsorption and about other properties.

III. EXPERIMENTAL WORK

A. Preparation of Finely Divided Nickel

Nickel of colloidal dimensions was prepared using high-surface sodium.[1] The apparatus employed was designed so that this sodium could be prepared and then used to produce the nickel in a single reaction vessel. A three-necked flask was used as the vessel. Through the center opening entered a pivoted semicircular glass stirring blade connected to a motor by a glass rod. A mercury-seal bearing prevented gas leaks. One of the side openings of the three-necked flask was used for the introduction of reactants. The third opening in the reaction vessel was equipped with a gas lock and was used for the addition of sodium. A rubber hose attached to this opening was opened and closed with a pinchclamp, which allowed the sodium to be kept in an inert atmosphere before and during addition into the reaction vessel. The reaction vessel was encased by a heating mantle and was provided with a thermocouple with which its temperature was determined.

The nickel preparation was accomplished as follows: the air in the reaction vessel was displaced by nitrogen, and this inert atmosphere was then maintained throughout the process by continuously admitting and venting more of the gas. Since sodium chloride was employed as the inert carrier for the high-surface sodium, 144 grams of dry sodium chloride was placed in the reaction flask through the addition tube. The temperature of the flask was raised to 150°-200° C., and approximately 2.5 grams of sodium was added. The sodium

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1 U. S. Industrial Chemicals Co., High Surface Sodium on Inert Solids. New York, 1953.

was dispersed on the surface of the salt by vigorous mixing of the sodium and the salt. After the sodium was dispersed and while the stirring continued, 10 grams of dried and finely powdered nickel chloride was added slowly. The temperature of the reaction vessel was then raised slowly to 250° C. and its contents were stirred at this temperature for one hour.

The product, consisting of sodium chloride, sodium and nickel metal, was cooled, and methanol was added to decompose the excess sodium. The remaining product was washed with water and decanted several times to remove the salt and was then filtered through a fritted glass disc. Methanol was again added to dissolve the sodium soap. The finely divided nickel was then dried in a vacuum oven. The specific surface area of a product compounded by mixing the products of a number of preparations was measured by low-temperature nitrogen gas adsorption and found to be 25.7 m^2/g.

B. Heat of Adsorption

1. Direct Measurement

Only one minor change has been made in the heat of adsorption apparatus which has been described previously.[2] A 9-mm.-O.D. tube leading directly to the high-vacuum manifold at the top of the apparatus was sealed onto the sample tube. Thus it became possible to evacuate the sample in less time than was formerly required because the gas removed during the evacuation period did not have to pass through the long, coiled tubing surrounding the sample tube.

Additional measurements were made of the heat of adsorption of nitrogen gas on the coconut charcoal also described previously.[3] The data resulting

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2 DallaValle, J. M., Orr, Clyde, Jr., and Blocker, H. G., Research on Surface Properties of Fine Particles. Final Report, Project No. 181-119, Contract No. DA-36-039-sc-5411, Georgia Institute of Technology, Atlanta, April 30, 1953.

3 Ibid.

from these measurements are presented in the appendix in Table II. The results calculated from them and from previous determinations are presented in Figure 1. Since the heat of adsorption measured by this method is the average heat liberated during one increment of gas admitted to the sample, the data were plotted as short lines whose length was estimated by the amount of gas adsorbed in each increment.

2. Calculation from Adsorption

a. Method. It is possible to calculate differential heats of adsorption by means of an equation developed by Clapeyron and later extended by Clausius. The form of this equation used by Hansen[4] is

$$\left(\frac{d \ln p}{dT}\right)_V = \frac{H_d}{RT^2} \qquad (1)$$

where p is the equilibrium pressure, V is the volume adsorbed at the temperature T and the pressure p, H_d is the differential heat of adsorption, and R is the gas constant. Substituting dp/p for d ln p and solving for H_d, the heat of adsorption is

$$H_d = \frac{RT^2}{p}\left(\frac{dp}{dT}\right)_V . \qquad (2)$$

Since the derivative must be evaluated with the volume adsorbed constant, it is necessary to obtain an adsorption isostere for each condition at which the heat of adsorption is to be determined. It was decided to determine these isosteres from several isotherms run at different temperatures.

Two procedures were employed in the treatment of the data. In the first, several adsorption isotherms for different temperatures were plotted (V as ordinate versus p as abscissa) on coordinate paper. The pressure on each of

4 Hansen, R. S., "Calculations of Heats of Adsorption from Adsorption Isosteres." J. Phys. Chem. 54, 411-15 (1950).

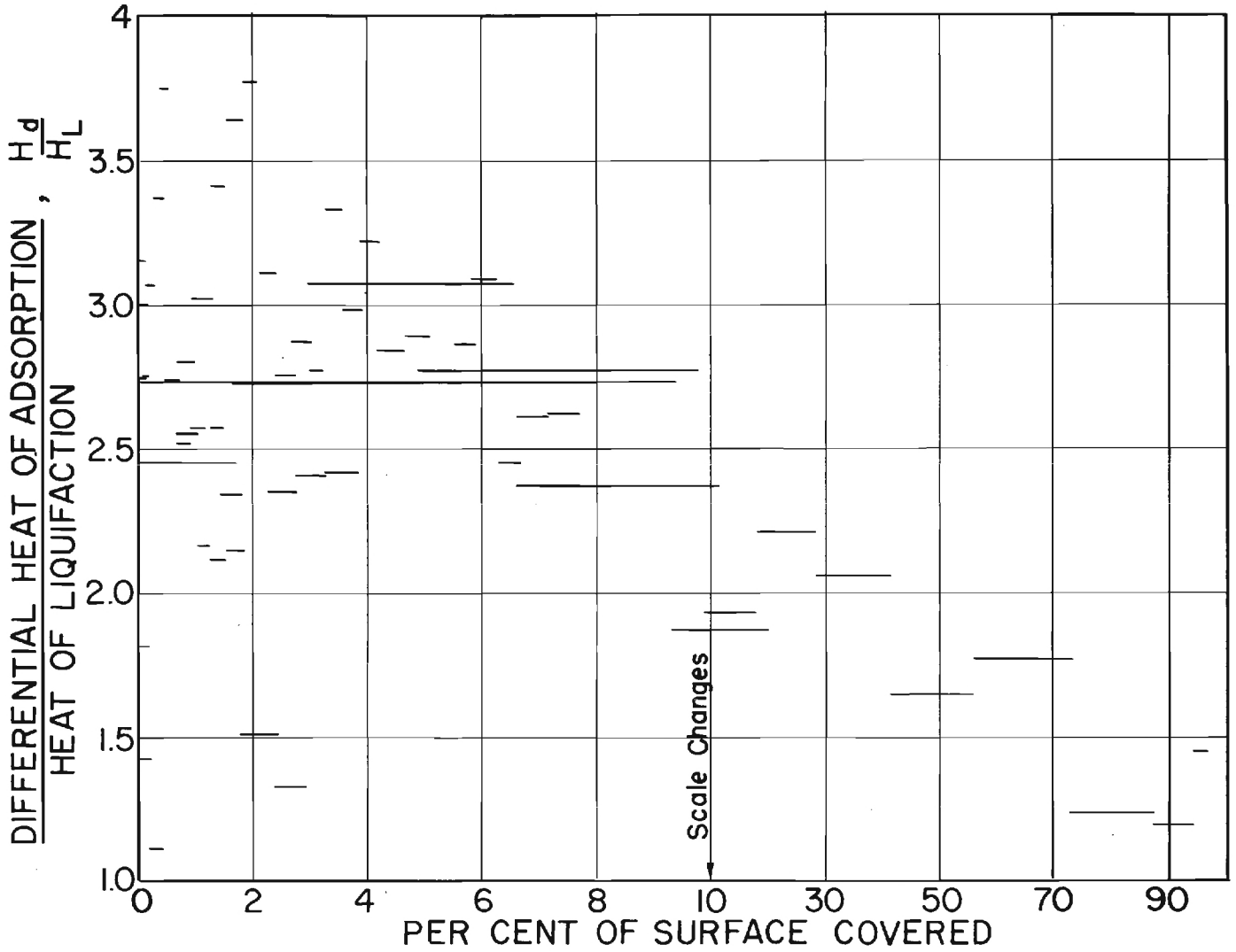

Figure 1. Heat of Adsorption as a Function of the Surface of Adsorbent Covered.

these isotherms was then determined for particular volumes of adsorbed gas, and these pressures were plotted against the corresponding temperatures of the isotherms. The resulting curve was an adsorption isostere from which the pressure, p, and the derivative $(dp/dT)_V$ were evaluated at particular temperatures. By means of equation 2, the differential heat of adsorption was then evaluated for a particular volume of gas adsorbed. The procedure was repeated at other volumes of adsorbed gas.

The second procedure required that the isostere be fitted by an equation derived from equation 2. This equation may be written

$$\frac{dp}{p} = \frac{H_d \, dT}{RT^2} \quad . \tag{3}$$

If the assumption is made that H_d is independent of T over the narrow limits of T employed in these measurements, equation 3 may be integrated giving

$$\ln p = C - \frac{H_d}{RT} \tag{4}$$

where C is a constant of integration. The value of H_d at each volume of adsorbed gas was determined by the method of least squares. The two simultaneous equations required to evaluate the constants C and H_d in equation 4 are

$$\begin{aligned} \Sigma \ln p &= Cn - \frac{H_d}{R} \Sigma \frac{1}{T} \\ \Sigma \frac{1}{T} \ln p &= C\Sigma \frac{1}{T} - \frac{H_d}{R} \Sigma \frac{1}{T^2} \quad , \end{aligned} \tag{5}$$

where n is the number of isotherms employed. Pressure and temperature measurements were taken directly from adsorption isotherms and equations 5 were solved for C and H_d/R, from which the differential heat of adsorption, H_d, was determined.

b. Apparatus. In order to obtain additional adsorption isotherms without interfering with the experimental determination of heats of adsorption, it was decided to construct a second low-temperature adsorption apparatus. A schematic drawing of the new apparatus is given in Figure 2. Three sample tubes were provided, each with three-way stopcocks, so that two samples could be evacuated while adsorption measurements were being made on the other sample.

The new adsorption apparatus was constructed with Pyrex glass tubing and standard-taper stopcocks with interchangeable plugs. Some difficulty was encountered with leaking stopcocks during the first attempts to use the equipment. The stopcocks were then lapped in with No. 400 and with No. 600 silicon carbide grit. The difficulty was greatly reduced.

The volumes of the connective tubing and of the sample tubes were determined by calibration with helium gas. Baths of liquid nitrogen and liquid nitrogen and oxygen mixtures were employed to cool the samples. The temperature of each bath was measured with an argon-vapor-pressure thermometer while the temperature of the burette space was measured with a mercury-in-glass-type thermometer. Pressures less than 2 mm. Hg were measured with a McLeod gauge provided with two different-sized capillaries mounted end-to-end. Pressures as low as 0.001 micron and as high as 2,000 microns can be measured with the gauge. A mercury manometer was used for measuring pressures from 2 to 800 mm. Hg.

c. Adsorption Procedure. The volume of gas adsorbed from each increment of gas admitted to the adsorption space was determined from a material balance of the gas in the space before and after the adsorption had taken place. Thus, referring to Figure 2,

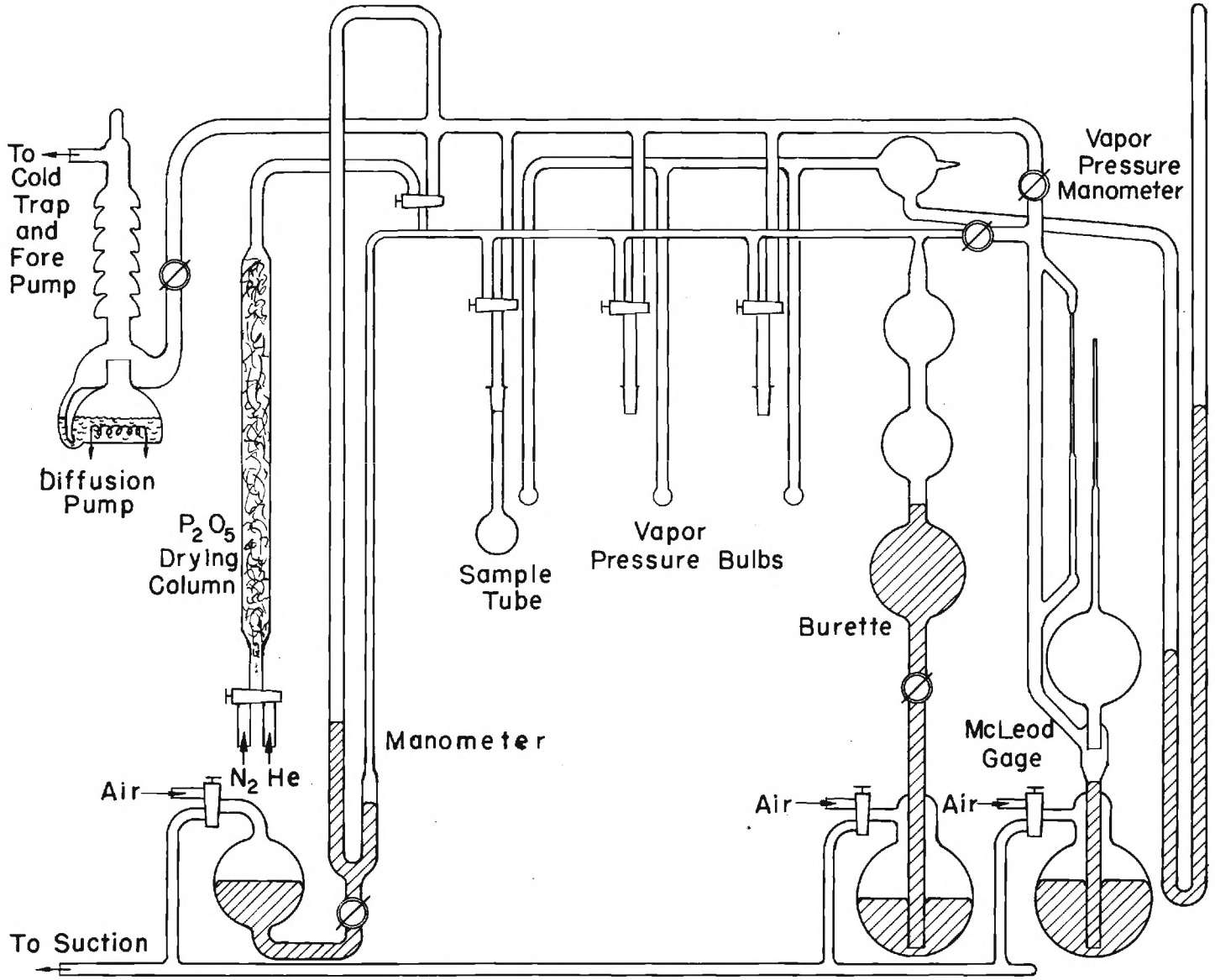

Figure 2. Schematic Diagram of Gas Apparatus.

$$\frac{p_1 V_t}{T_b} + \frac{p_o V_s (1 + \alpha p_o)}{T_s'} = \frac{p_2 V_t}{T_b} + \frac{p_2 V_s (1 + \alpha p_2)}{T_s'} + V_a \frac{760}{273} \qquad (6)$$

where p_o = initial pressure in sample tube, mm. Hg,

p_1 = initial pressure in burette space, mm. Hg,

p_2 = final pressure in burette space and sample tube, mm. Hg,

V_t = volume of burettes and connective tubing, ml.,

V_s = volume of sample tube, ml.,

V_a = volume of gas adsorbed, cc. at S.T.P.,

T_b = temperature of burettes, °K.,

T_s = temperature of liquid nitrogen bath, °K.,

T_s' = average temperature of sample tube, °K.,

α = correction for deviation of nitrogen from perfect gas law = 6.6×10^{-5} (mm. Hg)$^{-1}$.

Solving for the volume adsorbed,

$$V_a = \frac{273}{760} \left[\frac{V_t}{T_b}(p_1 - p_2) - \frac{V_s}{T_s'}(p_2 - p_o) - \alpha \frac{V_s}{T_s'}(p_2^2 - p_o^2) \right] . \qquad (7)$$

Samples were prepared for adsorption in the usual manner, i.e., by drying at 110° C. and cooling in a desiccator before weighing. They were prepared for adsorption by heating at 250°-300° C. while being evacuated to pressures of the order of 0.1 micron. The volume of the sample tube was determined with helium with the sample tube at room temperature.

Since the glass tubing between the sample stopcock and the sample is neither at the temperature of the sample nor at that of the surroundings, it is necessary to establish an effective or average, temperature for the sample tube. This was done by placing the liquid nitrogen bath about the sample tube in its normal position and then removing the bath while the sample tube still

contained the helium used in determining its volume. The average temperature was then found from material balances on the gas in the system when the bath was in place and after the bath had been removed, assuming helium to be not measurably adsorbed at liquid nitrogen temperature. This procedure was used exclusively in the case of the nickel powder.

There is some indication that helium may be adsorbed to an appreciable extent by some high-surface carbonaceous materials at the temperature of liquid nitrogen.[5] Indeed, this seems to be the case with the charcoal used in the measurements reported herein, because temperatures lower than that of the liquid nitrogen bath are obtained by the procedure outlined above. For this reason, the average temperature of the tube in the case of charcoal was estimated from the temperatures obtained with nickel as the adsorbent.

Changes in the temperature at which adsorption measurements were made were brought about by changing the percentages of oxygen and nitrogen in the liquid bath. Commercial liquid nitrogen gave the lowest temperature employed. Progressively higher temperatures were obtained by bubbling oxygen into this nearly pure nitrogen until the desired temperature was attained.

Isotherms were determined for the adsorption of nitrogen by colloidal nickel prepared by the high-surface-sodium method and for the acid-washed coconut charcoal, the preparation of which was described in a previous report.[6] These data are summarized in Table III in the appendix. Calculated heats of adsorption for various per cent coverages of the adsorbent surface are given in Table I.

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5 Beebe, R. A., Millard, B., and Cynarski, J., "Heats of Adsorption of Nitrogen and Argon on Porous and non-Porous Carbon Adsorbents at -195°." J. Am. Chem. Soc. 75, 839-45 (1953).

6 DallaValle, et al., op. cit.

TABLE I

CALCULATED HEATS OF ADSORPTION OF NITROGEN BY CHARCOAL AND POWDERED NICKEL

Material	T (°K.)	Surface Coverage (Per Cent)	H_d/H_L
Powdered Nickel	79	46.4	2.75
Powdered Nickel	79	55.7	3.10
Powdered Nickel	79	64.9	2.02
Powdered Nickel	79	74.2	1.71
Powdered Nickel	79	83.5	2.17
Powdered Nickel	79	92.8	1.86
Powdered Nickel	79	102.0	1.79
Powdered Nickel	79	111.3	1.95
Powdered Nickel	79	120.5	1.80
Powdered Nickel	79	129.9	1.63
Charcoal	77-83	11.8	2.98
Charcoal	77-83	23.7	2.32
Charcoal	77-83	35.5	2.80
Charcoal	77-83	47.3	2.97
Charcoal	77-83	59.2	3.77
Charcoal	77-83	71.0	3.08
Charcoal	77-83	82.8	2.05
Charcoal	77-83	88.8	0.95

IV. DISCUSSION OF RESULTS

A. Finely Divided Nickel

The specific surface area of the nickel produced by the sodium-reduction method proved not to be as great as had been hoped. This, of course, made the material less attractive as an adsorbent than it might have been, but the nickel has been used nevertheless. In some respects, the results obtained with nickel appear to be more consistent than those with charcoal.

B. Heat of Adsorption

1. Direct Measurement

Figure 1 permits visual evaluation of all of the heat of adsorption data for charcoal obtained by direct measurement. Considerable spread in the results is obvious; the reason for the spread is not as obvious. While some of the discrepancies are undoubtedly due to experimental error, it is believed that this is not the only source, because the experimental data, when plotted as shown in Figure 9 of a previous report,[7] consistently gave very smooth curves. The temperature to which the adsorbent was heated, the duration of the heating and the pressure of the evacuation are all believed to affect the course of the adsorption. Sufficient data to determine the effect of each of these factors have not been obtained.

2. Calculation from Measurement of Adsorption

The heats of adsorption obtained from adsorption isotherms as functions of the per cent of the adsorbent surface covered are presented in Table I. In general, the results for charcoal agree with those obtained by direct measurement, and those for nickel are of the order of magnitude expected.

7 DallaValle, et al., op. cit.

The charcoal results were obtained by the least-squares method outlined above; the nickel results were obtained by the simpler graphical analysis.

It was necessary to apply the mathematical analysis to the data for charcoal because of the scatter of the isosteric data. These data were scattered because they originated from differences in the adsorption isotherms which were quite small. As in the case of direct measurement of heat of adsorption, it is believed that the conditions of evacuation have some effect on heats of adsorption. It is possible that equilibrium pressures were not reached for some points, since the pressure change with time becomes quite low for charcoal. These and other minor inaccuracies, while entirely negligible for most purposes, may prove to be quite important in these measurements. The adsorption data did show small irregularities, but a plot of these data in accordance with the BET equation,[8] Figure 3, showed them to be quite consistent by previous standards.

V. FUTURE WORK

Contemplated studies will be concerned with the effects of heating and evacuating conditions on heats of adsorption. This problem will be approached by exposing several samples to as nearly identical conditions as possible and then measuring their adsorption characteristics at different temperatures. In general, experiments will be designed to eliminate as many variables as possible in order to obtain consistent data. Larger temperature differences will be employed in obtaining adsorption isotherms intended for use with the Clapeyron equation. Attempts will be continued to obtain heat of adsorption

8 Brunauer, S., Emmett, P. H., and Teller, E., "Adsorption of Gases in Multimolecular Layers." J. Am. Chem. Soc. 60, 309-19 (1938).

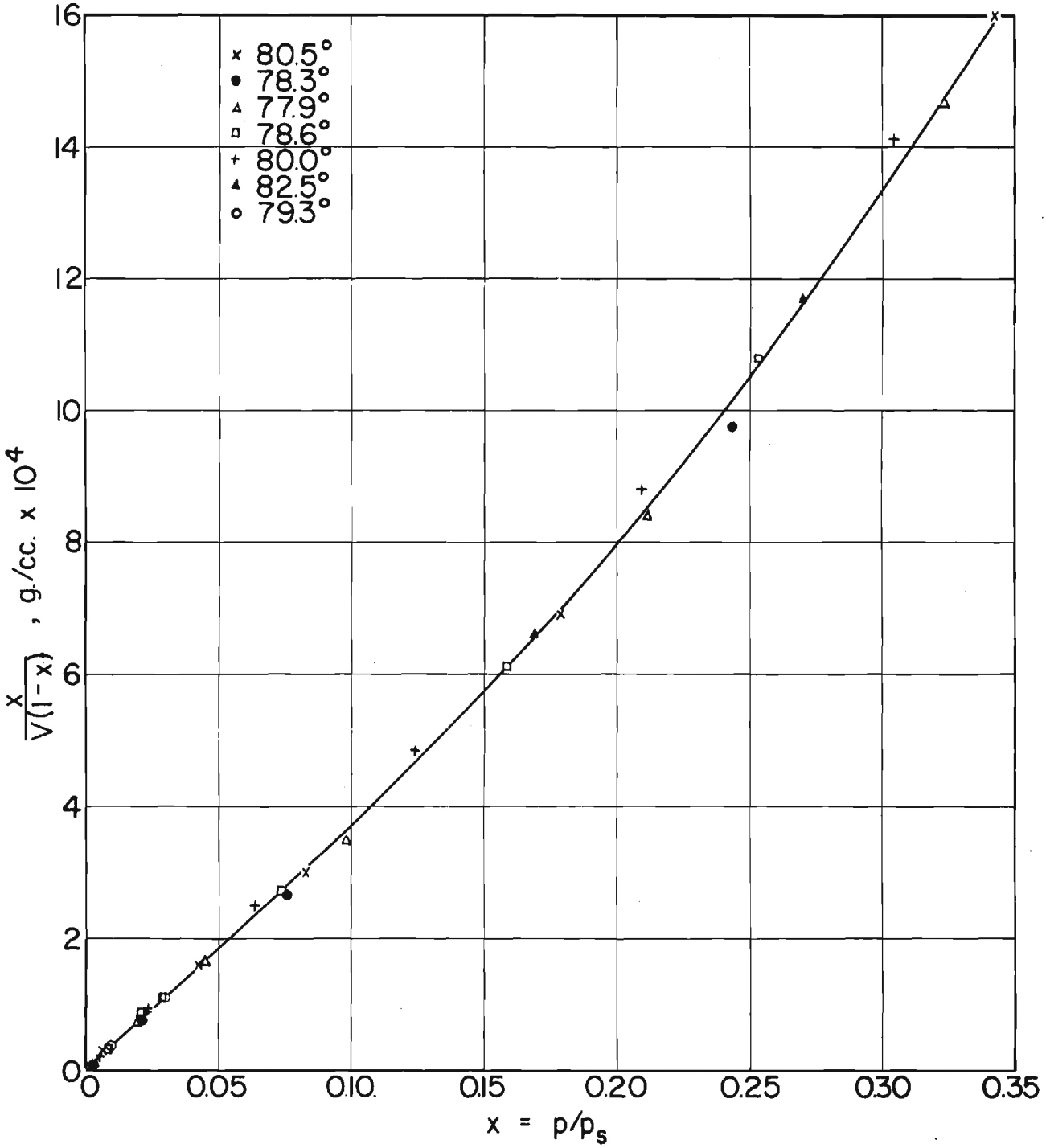

Figure 3. Adsorption of Nitrogen by Charcoal at Various Temperatures.

data when very small fractions of the adsorbent's surface are covered with adsorbed molecules.

VI. PERSONNEL

The technical personnel who worked on this project and the percentage of working time each devoted to the project during the period covered by this report are shown below:

Name	Title	Percentage of Working Time Devoted to Project
J. M. DallaValle	Project Director (Until October 15, 1953)	36
Clyde Orr, Jr.	Research Engineer (Until October 15, 1953)	39
H. G. Blocker	Research Engineer	94
Miss Jane Barrett	Research Assistant	44

Respectfully submitted:

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Clyde Orr, Jr.,
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H. G. Blocker

H. G. Blocker,
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D. Jane Barrett

D. Jane Barrett,
Research Assistant

Approved:

Herschel H. Cudd

Herschel H. Cudd, Director
Engineering Experiment Station

VII. APPENDIX

TABLE II

HEAT OF ADSORPTION DATA

P_1 (mm. Hg)	p (mm. Hg)	V (cc./g.)	H_d $\left(\frac{Cal.}{g.}\right)$	T_b (°K)	T_s (°K)	T_e (°K)	Constants
Charcoal:*							
29.8	0.0	0.273	---	303	78.50	287	w = 8.456 g.
26.0	0.0	0.511	0.165	303	78.50	287	V_t = 65.2 cc.
38.2	0.0	0.861	1.286	302	78.85	287	V_e = 3.0 cc.
47.3	0.0	1.295	1.067	302	78.85	287	V_s = 68.0 cc.
47.3	0.0	1.729	0.226	302	78.85	287	
67.7	0.0	2.348	0.165	303	78.93	287	
71.3	0.0	3.000	0.152	303	79.16	287	
64.0	0.0	3.585	0.155	303	79.16	287	
71.0	0.0	4.234	0.130	303	79.16	287	
62.9	0.0	4.809	0.155	303	79.16	287	
117.2	0.0	5.881	0.141	303	79.16	287	
205.8	0.0	7.763	0.091	303	79.3	287	
222.0	0.0	9.793	0.080	303	79.3	287	
Coconut Charcoal:**							
50.0	0.0	0.458	0.1892	302	77.9	286	w = 8.456 g.
55.4	0.0	0.966	0.1846	302	77.9	286	V_t = 65.2 cc.
61.2	0.0	1.527	0.2023	302	77.9	286	V_e = 3 cc.
90.2	0.0	2.354	0.1648	302	77.9	286	V_s = 67.6 cc.
94.9	0.0	3.224	0.1685	302	77.9	286	
115.0	0.0	4.279	0.1815	302	77.9	286	
93.6	0.0	5.137	0.2048	302	78.0	286	
108.8	0.0	6.135	0.2187	302	78.0	286	
107.7	0.0	7.123	0.1667	302	78.0	286	
107.1	0.0	8.105	0.1870	302	78.0	286	
112.9	0.0	9.140	0.1660	302	78.0	286	
104.8	0.0	10.101	0.1722	302	78.0	286	
105.8	0.0	11.071	0.1665	302	78.0	286	
111.8	0.0	12.096	0.1999	302	78.1	286	
106.9	0.0	13.076	0.1793	302	78.1	286	
116.0	0.0	14.139	0.1935	302	78.1	286	
160.0	0.0	15.606	0.1708	302	78.1	286	
158.5	0.0	17.055	0.1735	302	78.1	286	
152.0	0.0	18.457	---	302	78.1	286	

(Continued)

TABLE II (Continued)

HEAT OF ADSORPTION DATA

P_1 (mm. Hg)	p (mm. Hg)	V (cc./g.)	H_d $\left(\frac{Cal.}{g.}\right)$	T_b (°K)	T_s (°K)	T_e (°K)	Constants
Coconut Charcoal (Continued):							
150.0	0.0	19.833	0.1718	302	78.1	286	
153.4	0.0	21.240	0.1859	302	78.1	286	
132.8	0.0	22.458	0.1475	302	78.1	286	
184.8	0.0	24.153	0.1571	302	78.1	286	
133.0	0.0	25.373	0.1576	302	78.1	286	

*Acid-washed, evacuated 24 hours at 450° C. to 0.05μ pressure.

**Acid-washed, evacuated 48 hours at 400° C. to 0.01μ pressure.

TABLE III

EXPERIMENTAL NITROGEN GAS ADSORPTION DATA

p_1 (mm. Hg)	p (mm. Hg)	V (cc./g.)	Constants*
1. Coconut Charcoal:**			
143.2	0.00	8.95	w = 2.092 g.
197.1	0.00	21.27	T_b = 304.3° K
223.0	0.00	35.20	T_s = 79.3° K
270.3	0.00	52.09	T_s' = 95.0° K
234.6	0.00	66.74	V_s = 9.9 cc.
309.5	0.00	86.08	V_t = 110.9 cc.,
324.3	0.00	106.34	135.8 cc.
415.7	0.00	132.31	
443.0	0.10	159.98	
318.2	0.35	184.32	
348.7	1.09	210.92	
360.9	3.3	233.24	
326.0	9.4	252.91	
433.9	28.7	277.88	
2. Coconut Charcoal:			
273.9	0.050	36.4	w = 2.092 g.
204.1	0.071	63.5	T_b = 304.5° K
208.8	0.095	91.3	T_s = 80.5° K
214.0	0.124	119.8	T_s' = 95.0° K
234.8	0.197	151.5	V_s = 10.0 cc.
227.7	0.43	181.9	V_t = 235.8 cc.,
239.0	1.7	211.0	210.9 cc.
233.0	6.5	238.0	
250.0	22.1	264.9	
207.1	46.3	283.7	
240.9	90.2	300.9	
336.8	195.5	315.9	
471.3	373.0	324.6	

(Continued)

TABLE III (Continued)

EXPERIMENTAL NITROGEN GAS ADSORPTION DATA

P_1 (mm. Hg)	p (mm. Hg)	V (cc./g.)	Constants*
3. Coconut Charcoal:			
208.2	0.0018	16.15	w = 2.092 g.
236.5	0.0052	47.98	T_b = 301.0° K
241.2	0.0130	80.45	T_s = 78.3° K
250.0	0.0238	114.20	T_s' = 95.0° K
281.5	0.064	152.20	V_s = 10.0 cc.
346.0	0.034	198.87	V_t = 235.9 cc., 212.5 cc.
318.3	2.8	241.46	
314.6	18.5	277.10	
337.2	64.9	309.29	
398.9	209.8	329.58	
454.1	370.5	336.71	
4. Coconut Charcoal:			
206.1	0.0024	27.73	w = 2.029 g.
211.2	0.0055	56.01	T_b = 302.5° K
226.7	0.0143	86.37	T_s = 79.2° K
237.0	0.032	118.10	T_s' = 95.0° K
243.4	0.089	150.69	V_s = 10.0 cc.
249.4	0.280	184.04	V_t = 235.8 cc.
272.0	1.80	220.19	
5. Coconut Charcoal:			
201.4	0.0068	26.754	w = 2.1259 g.
202.8	0.0145	53.694	T_b = 300° K
211.4	0.0280	81.776	T_s = 78.6° K
218.4	0.0480	110.788	T_s' = 95° K
222.2	0.0950	140.291	V_s = 9.8 cc.
230.0	0.270	170.802	V_t = 235.8 cc., 210.9 cc.
225.8	1.26	200.637	
259.2	7.0	234.037	
255.5	25.4	264.283	
273.2	66.1	291.083	
278.4	141.5	307.942	
290.0	226.0	314.941	

(Continued)

TABLE III (Continued)

EXPERIMENTAL NITROGEN GAS ADSORPTION DATA

p_1 (mm. Hg)	p (mm. Hg)	V (cc./g.)	Constants*
6. Coconut Charcoal:			
246.0	0.0030	32.99	w = 2.092 g.
248.9	0.0080	66.37	T_b = 302° K,
249.0	0.0180	99.76	301.5° K
262.7	0.0450	134.99	T_s = 77.9° K,
245.0	0.113	167.83	78.0° K
298.7	0.620	207.79	T_s' = 95° K
			V_s = 10.0 cc.
301.6	6.0	247.33	V_t = 235.8 cc.,
200.5	15.7	269.25	210.9 cc.
215.0	36.8	289.98	
241.8	80.2	308.55	
294.0	174.0	321.24	
325.8	266.3	326.67	
392.0	350.3	330.10	
7. Coconut Charcoal:			
205.5	0.0140	27.444	w = 2.1253 g.
230.8	0.039	58.267	T_b = 298.5° K,
228.5	0.067	88.769	301° K
261.3	0.150	123.651	T_s = 80.0° K,
264.0	0.245	158.879	80.3° K
277.5	1.065	191.605	T_s' = 95° K
			V_s = 10.1 cc.
279.9	5.9	223.974	V_t = 235.8 cc.,
265.3	24.2	252.204	210.9 cc.
271.1	64.9	275.895	
269.9	125.0	291.967	
294.7	207.2	300.825	
368.0	307.0	306.200	

(Continued)

TABLE III (Continued)

EXPERIMENTAL NITROGEN GAS ADSORPTION DATA

p_1 (mm. Hg)	p (mm. Hg)	V (cc./g.)	Constants*
8. Coconut Charcoal:			
215.5	0.0026	28.64	w = 2.1292 g.
315.0	0.0171	70.56	T_b = 299° K,
342.5	0.070	116.14	298° K
375.0	0.425	166.04	T_s = 82.5° K
359.7	4.0	213.27	T_s' = 95° K
			V_s = 17.12 cc.
296.1	22.0	249.20	V_t = 235.8 cc.,
368.0	81.1	285.57	210.9 cc.
366.5	181.5	307.19	
388.4	289.6	316.99	
9. Nickel Powder:***			
54.9	0.042	1.190	w = 7.44 g.
90.7	2.7	3.037	T_b = 302.5° K
			T_s = 77.9° K
93.2	6.0	3.810	T_s' = 81.1° K
124.2	13.9	4.703	V_s = 38.1 cc.
159.0	31.2	5.552	V_t = 135.8 cc.,
193.9	63.4	6.085	60.9 cc.
241.2	97.5	6.701	
274.5	134.1	7.223	
316.2	171.5	7.764	
356.7	208.2	8.353	
378.0	243.2	8.856	
10. Nickel Powder:			
83.9	0.400	1.816	w = 7.44 g.
94.5	6.1	3.631	T_b = 300.3° K
			T_s = 80.0° K
107.1	12.7	4.421	T_s' = 83.0° K
125.0	25.6	5.131	V_s = 38.1 cc.
160.0	48.0	5.770	V_t = 135.8 cc.,
191.7	76.9	6.302	60.9 cc.
246.2	112.6	6.815	
302.0	154.1	7.464	
357.0	197.2	8.132	

(Continued)

TABLE III (Continued)

EXPERIMENTAL NITROGEN GAS ADSORPTION DATA

p_1 (mm. Hg)	p (mm. Hg)	V (cc./g.)	Constants*
11. Nickel Powder:			
18.9	0.0105	0.407	w = 7.440 g.
27.0	0.0260	0.985	T_b = 300° K,
			301° K,
34.9	2.2	1.269	302°K
50.1	5.2	1.645	T_s = 83.0° K
72.0	11.5	2.104	T_s' = 86.7° K
			V_s = 38.2 cc.
95.8	23.0	2.572	V_t = 135.8 cc.,
111.0	39.1	2.933	60.9 cc.
142.9	61.5	3.251	60.9 cc.
174.0	88.5	3.505	
205.0	116.0	3.782	
230.7	147.9	3.900	
274.0	178.9	4.152	
330.2	218.0	4.391	
380.7	261.9	4.584	
455.1	312.5	4.855	
554.0	373.5	5.256	
12. Nickel Powder:			
23.1	0.0020	0.502	w = 7.440 g.
22.9	0.0110	0.999	T_b = 302.0°K
32.9	0.040	1.712	T_s = 78.0° K
28.0	0.370	2.305	T_s' = 79.5° K
28.0	1.38	2.860	V_s = 37.9 cc.
			V_t = 135.8 cc.,
55.9	3.0	3.338	60.9 cc.
52.1	4.9	3.754	
69.9	8.3	4.275	
74.7	14.1	4.732	
97.1	25.0	5.184	
103.8	38.2	5.518	
142.7	58.1	5.881	
170.5	81.1	6.217	
219.4	109.7	6.619	
264.1	141.6	7.066	
302.9	175.3	7.518	

(Continued)

TABLE III (Continued)

EXPERIMENTAL NITROGEN GAS ADSORPTION DATA

P_1 (mm. Hg)	p (mm. Hg)	V (cc./g.)	Constants*
13. Nickel Powder:			
27.7	0.0076	0.602	w = 7.440 g.
32.2	0.050	1.300	T_b = 302.0° K,
35.0	0.349	2.047	303.0° K
36.3	1.65	2.772	T_s = 80.0° K
			T_s' = 82.6° K
53.6	4.0	3.202	V_s = 37.9 cc.
71.1	7.1	3.736	V_t = 135.8 cc.,
90.8	14.5	4.313	60.9 cc.
111.8	28.1	4.824	
126.4	44.2	5.264	
138.2	63.8	5.549	
158.0	84.7	5.793	
14. Nickel Powder:			
29.3	0.040	0.643	w = 7.440 g.
32.2	0.735	1.333	T_b = 299° K,
			300° K
60.0	3.0	1.842	T_s = 82.0° K
64.9	7.9	2.295	T_s' = 85.2° K
68.3	13.1	2.723	V_s = 32.2 cc.
83.4	23.9	3.070	V_t = 135.8 cc.,
86.0	34.9	3.332	60.9 cc.
106.5	49.9	3.560	
128.9	67.0	3.793	
152.3	88.0	3.963	
192.0	114.0	4.156	
211.2	139.0	4.313	
258.5	169.3	4.517	
309.0	203.1	4.805	
362.8	245.0	5.024	

(Continued)

TABLE III (Concluded)

EXPERIMENTAL NITROGEN GAS ADSORPTION DATA

P_1 (mm. Hg)	p (mm. Hg)	V (cc./g.)	Constants*
15. Nickel Powder:			
458.1	19.0	3.7344	w = 7.440 g.
201.7	50.8	4.4951	T_b = 303.6° K
258.0	96.0	5.0632	T_s = 80.8° K
330.3	151.0	5.5740	T_s' = 84.2° K
406.6	212.8	6.0629	V_s = 38.2 cc.
462.5	272.4	6.5552	V_t = 60.9 cc.
523.0	330.7	7.0882	
583.1	389.6	7.6091	
705.3	458.0	8.4202	

* When more than one value is given for a constant, the first value refers to the first group of data, the second to the second group, etc.

** Descriptions of coconut charcoals:

1. Evacuated 20 hrs. at 300° C. to 0.3μ pressure.
2. Evacuated 18 hrs. at 300° C. to 0.1μ pressure.
3. Evacuated 20 hrs. at 300° C. to 0.1μ pressure.
4. Evacuated 20 hrs. at 375° C. to 0.001μ pressure.
5. Evacuated 20 hrs. at 300° C. to 0.01μ pressure.
6. Evacuated 24 hrs. at 375° C. to 0.04μ pressure.
7. Evacuated 24 hrs. at 375° C. to 0.04μ pressure.
8. Evacuated 24 hrs. at 375° C. to 0.04μ pressure.

*** Descriptions of nickel powders:

9. Colloidal-HSS technique.
10. Colloidal-HSS technique.
11. Colloidal-HSS technique.
12. Colloidal, evacuated 20 hrs. at 300° C. to 0.001μ pressure.
13. Colloidal-HSS technique. Exposed to air, then evacuated 20 hrs. at 250° C. to 0.1μ pressure.
14. Colloidal-HSS technique.
15. Colloidal-HSS technique.

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

QUARTERLY REPORT NO. 3

PROJECT NO. 228-197

STANDARDIZATION OF SURFACE PROPERTIES OF FINE PARTICLES

By

CLYDE ORR, JR., H. G. BLOCKER,
and D. JANE BARRETT

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CONTRACT NO. DA-36-039-sc-42588

DEPARTMENT OF THE ARMY PROJECT: 3-99-15-022
SIGNAL CORPS PROJECT: 152B

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JANUARY 30, 1954

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I. ABSTRACT

The general purpose of this investigation is an evaluation of the surface properties of finely divided solid materials. The present study is concerned primarily with heats of adsorption, i.e., the heat released at a solid's surface when a gas comes into contact with the solid.

The work of this report period has dealt almost entirely with refinements in apparatus and technique, since acceptable heat of adsorption data requires precision work. Particular attention has been given to the purification of the gases used, to the purification of the surface upon which adsorption occurred and to the accurate measurement of pressure. Unsolved problems involve the regulation of the adsorbent temperature at several levels of temperature and minor leaks attributable to glass stopcocks. Major sources of error are believed to be overcome, however.

In the time remaining, as much heat of adsorption information as possible will be collected.

II. PURPOSE

An evaluation of the surface properties of finely divided solid materials such that the standardization of these properties may be attained is the ultimate goal of this investigation. Currently, the phenomenon being studied is the heat resulting when a gas comes into contact with a solid surface which is not contaminated from previous contacts with gases.

This phenomenon of heat of adsorption has long been known. Because of the relatively small quantity of heat which must be measured, few quantitative measurements have been made, however, and some of these are of questionable value. Accurate measurements will permit a better understanding of the structure of solids, of the role of catalysts in chemical reactions and of adsorption in general.

The work accomplished during this report period has dealt with changes designed to increase the accuracy of the measurements. The highest accuracy attainable is necessary, since final results must be obtained from small differences among rather large quantities.

III. EXPERIMENTAL WORK

A. Apparatus

1. Gas Purification

Commercial oil-pumped nitrogen gas has been used as the adsorbate in all adsorption experiments made so far under this contract. Emmett[1] has stated that the small fractions of impurities in this nitrogen, primarily oxygen and the rare gases, do not interfere with adsorption measurements designed for surface area determinations unless the materials combine chemically with the oxygen at low temperatures. However, since very small changes in the quantity of gas adsorbed are important when measuring heats of adsorption, these impurities must be removed for heat-of-adsorption studies.

The adsorption apparatus described in the previous report has been altered several times in order to increase the purity of the gases admitted to the sample and, thereby, to increase the accuracy of adsorption measurements. A photograph of the apparatus is shown in Figure 1. This photograph was made before the neon removal system, as finally designed, was installed. A drawing of the latest apparatus is given in Figure 2.

The apparatus was first altered as described below. Oxygen was removed from tank nitrogen by passing the gas through a column containing minus

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[1] Emmett, P. H., "A New Method for Measuring the Surface Areas of Finely Divided Materials and for Determining the Size of Particles." Symposium on New Methods for Size Determination in the Subsieve Range, A.S.T.M. Philadelphia, March 4, 1941.

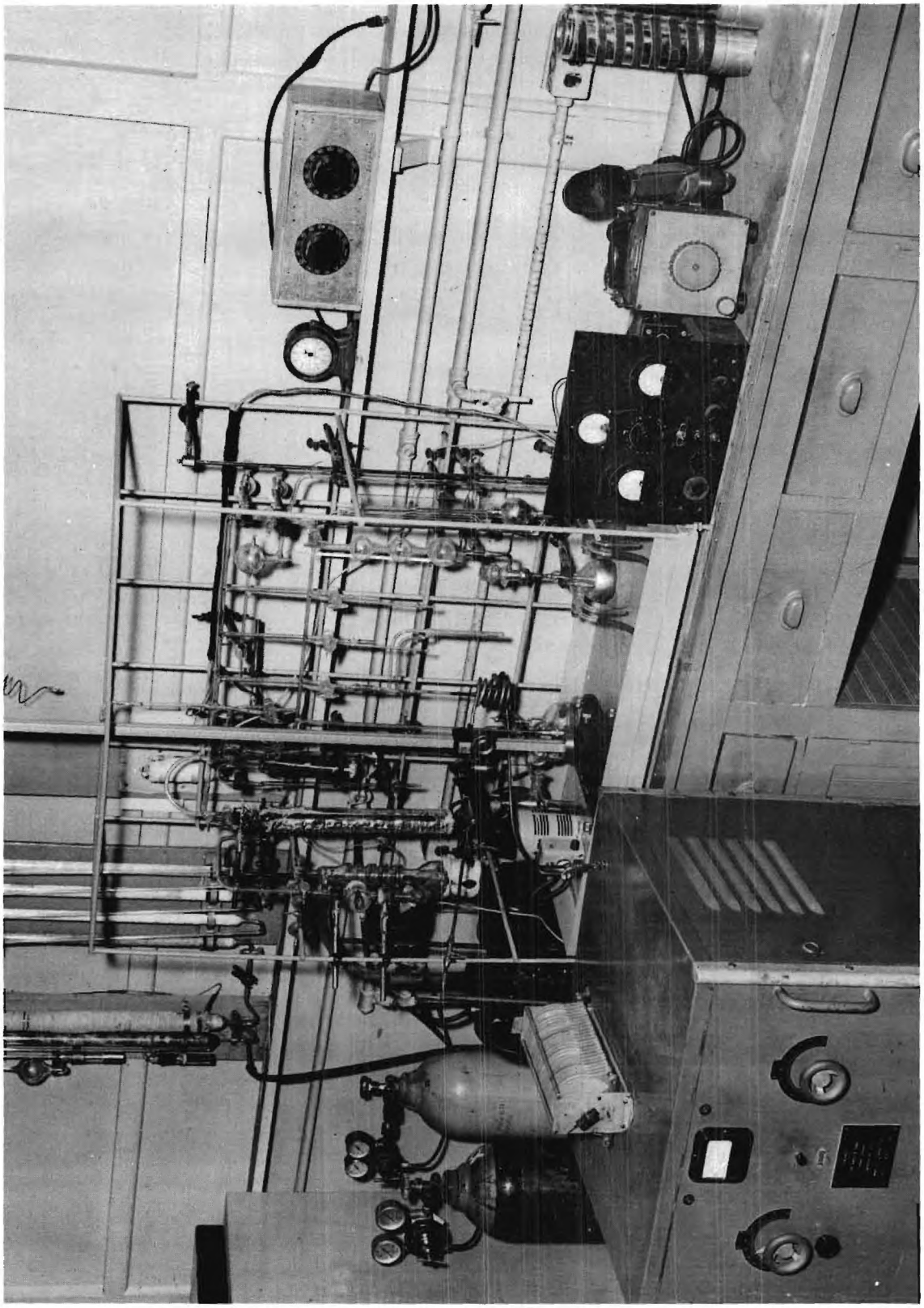

Figure 1. Heat of Adsorption Apparatus.

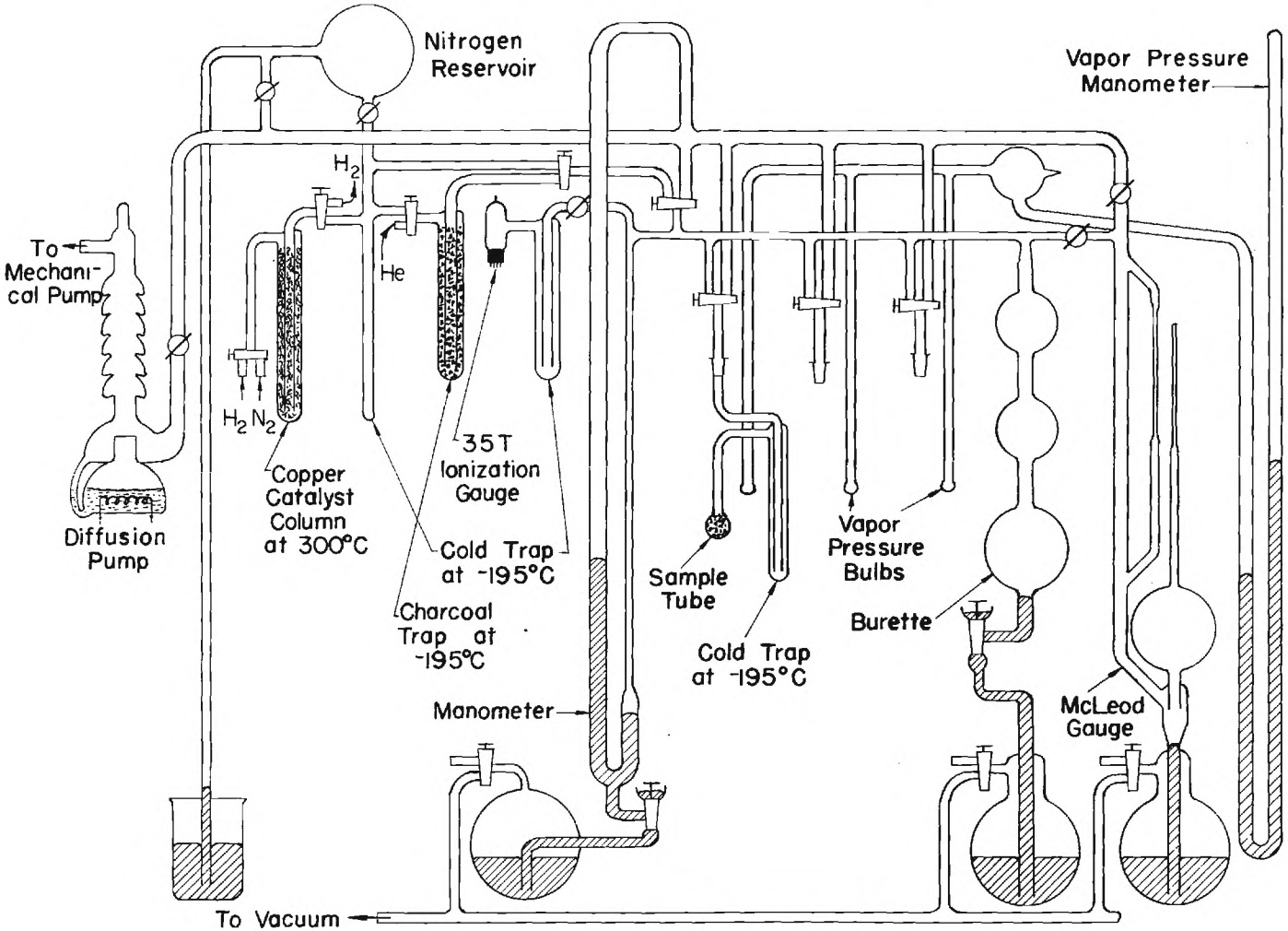

Figure 2. Schematic Diagram of Heat of Adsorption Apparatus.

100-mesh copper powder compressed into minus 20- and plus 80-mesh aggregates and heated to 300° C. The copper was reduced with hydrogen at 300° C prior to passing the gas to be purified through the column. The nitrogen was passed through a charcoal trap similar to that used for helium just prior to adsorption. This procedure would have been satisfactory if only oxygen, hydrogen and condensable gases had been present. As discovered later, a significant quantity of some of the rarer gases was present. The charcoal trap as used, therefore, actually concentrated the rarer gases rather than removed them because nitrogen gas would be adsorbed while the rare gases would not be adsorbed to any great extent. The apparatus and the technique of nitrogen purification were subsequently altered in order to remove neon and other nonadsorbable gases. One of the charcoal traps was replaced with a vertical condensation tube above which a five-liter flask was installed. Appropriate stopcocks and connective tubing for evacuating each part of the purification system separately were provided. This system is shown in Figure 2. The charcoal trap is cooled and nitrogen gas is adsorbed on the charcoal. Nonadsorbed gases are then pumped out, and the temperature of the charcoal trap is allowed to rise to that of the room, while the condensation tube is cooled with liquid nitrogen to condense the desorbing nitrogen. The process is repeated if necessary until sufficiently pure nitrogen is obtained, which may be stored in the five-liter nitrogen reservoir until it is used.

In order to protect the sample from contamination by the mercury and stopcock grease vapors, a liquid nitrogen trap was incorporated between the sample space and the other parts of the system.

The average temperature of the sample space, when obtained by expanding a known volume of helium into the cooled sample space and calculating the temperature from the pressure change, was found to be slightly lower than the temperature of the liquid nitrogen bath surrounding the sample space as indicated by an argon vapor pressure thermometer. This lower temperature was thought at first to have been due to the adsorption of helium by the charcoal, since an indication of such adsorption by high-surface carbonaceous materials has been reported by Beebe, Millard and Cynarski.[2] The same effect could have been produced by the adsorption of impurities from the helium. Therefore, it was decided to purify the helium further by passing it through a degassed charcoal trap at liquid nitrogen temperature before expanding it into the sample space. It is believed that by this method essentially pure helium was obtained. A sample space temperature slightly above that of the liquid nitrogen bath was obtained after such purification.

2. Pressure Measurement

Measuring the low pressures encountered causes much of the difficulty in obtaining accurate adsorption data. Several changes in the apparatus were made to increase the accuracy of pressure measurements. The small diameter tubing used for a manometer in the original apparatus (Figure 2, Quarterly Report No. 2) was replaced by larger tubing to minimize capillarity effects, and to reduce the error caused by the adhesion of mercury to the manometer wall. In the original manometer, pressures were measured by adjusting the mercury level in one leg of the manometer to a zero mark on the tubing and

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[2] Beebe, R. A., Millard, B., and Cynarski, J., "Heats of Adsorption of Nitrogen and Argon on Porous and Non-Porous Carbon Adsorbents at -195°." J. Am. Chem. Soc. 75, 839-45 (1953).

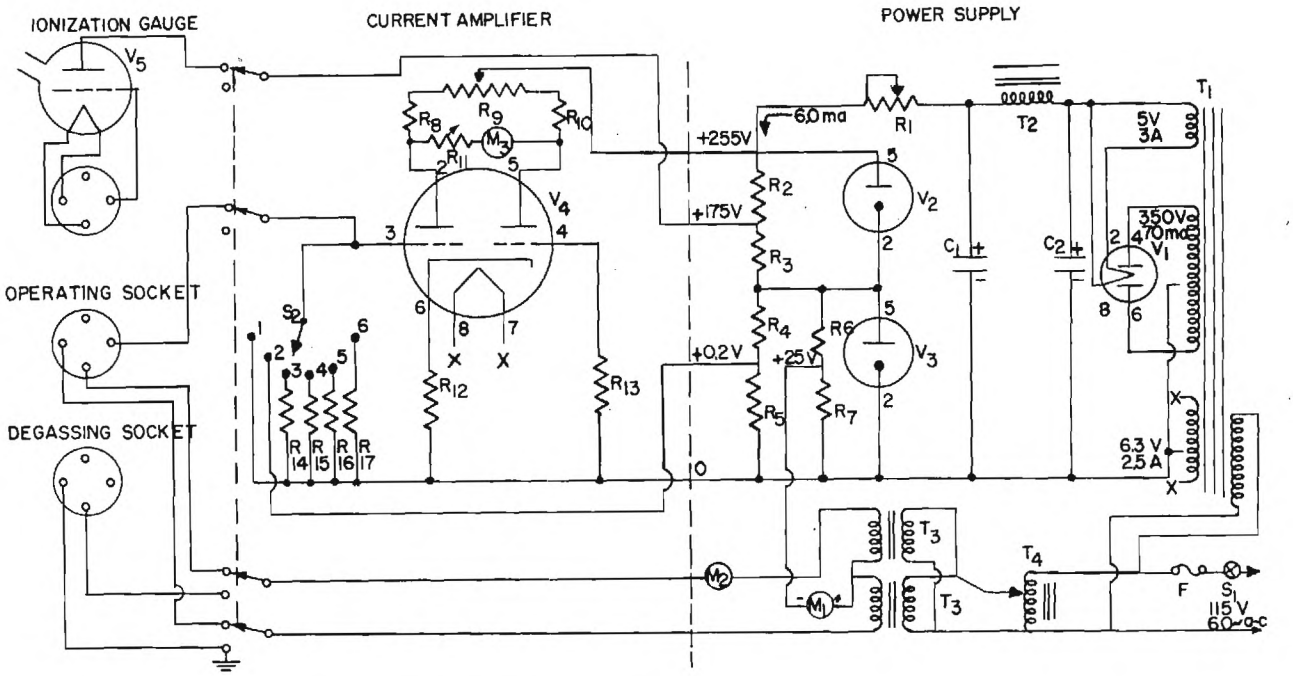
reading the height of the mercury column in the left leg by means of lines etched on the glass tubing. With the larger diameter manometer tube, pressures are measured with the aid of a cathetometer. This device was constructed of parts from a commercial cathetometer and of specially designed parts. It is shown in Figure 1. The cathetometer has a twenty-power telescope which may be rotated about a vertical axis and focused on the top of the meniscus in either leg of the manometer. The height of the mercury is measured with a vernier scale which may be read directly to 0.1 mm. over the pressure range 0 to 800 mm. For more accurate measurement of pressures up to 100 mm., the height of the telescope above the base of the cathetometer may be measured with a micrometer to within 0.0005 inch or approximately 0.01 mm.

An ionization gauge was installed in order that continuous readings could be made in the pressure range 0 to 0.005 mm. The gauge, an Eitel-McCullough, Inc., San Bruno, California, type 35T tube, was connected to the adsorption space through a stopcock and a liquid nitrogen trap to protect the tube from mercury vapor. The circuit of its power supply and amplifier is shown in Figure 3.

Degassing of the ionization gauge was accomplished by applying 1,500 volts dc from an external source to the plate of the ionization gauge and increasing the filament voltage until the plate became cherry red. Provision was made for grounding the filament and disconnecting the grid during degassing. The tube was evacuated to a pressure of about 0.2 micron while being heated. No changes were made in the McLeod gauge employed previously for pressure measurements.

3. Sample Preparation

An induction heater has been set up for more thorough degassing of the adsorption sample than has formerly been possible. A model 2 dielectric



C_1 30 μfd ELECTROLYTIC, 450 VOLTS
C_2 30 μfd ELECTROLYTIC, 450 VOLTS
R_1 3,000 OHMS, 5 WATTS
R_2 2,250 OHMS, 5 WATTS
R_3 2,500 OHMS, 2 WATTS
R_4 4,000 OHMS, 2 WATTS
R_5 950 OHMS, 2 WATTS
R_6 20,000 OHMS, 2 WATTS
R_7 38 OHMS, 2 WATTS
R_8 10,000 OHMS, 2 WATTS
R_9 5,000 OHMS, 4 WATTS
R_{10} 10,000 OHMS, 2 WATTS
R_{11} 25,000 OHMS, 4 WATTS, WIRE-WOUND
R_{12} 2,000 OHMS, 2 WATTS
R_{13} 2 MEGOHMS, 1 WATT
R_{14} 2,000 OHMS, 1 WATT, WIRE-WOUND PRECISION
R_{15} 20,000 OHMS, 1 WATT, WIRE-WOUND PRECISION
R_{16} 200,000 OHMS, 1 WATT, WIRE-WOUND PRECISION
R_{17} 2 MEGOHMS, 2 WATTS, WIRE-WOUND PRECISION

T_1 POWER TRANSFORMER (THORDARSON T-13R12 OR EQUIVALENT)
T_2 CHOKE, 10H, 110 MA (THORDARSON T-57054 OR EQUIVALENT)
T_3 FILAMENT TRANSFORMER, 5 VOLTS, 4 AMPS (THORDARSON T-63F99 OR EQUIVALENT)
T_4 1-AMP VARIAC, TYPE 200-B
V_1 5U4-G
V_2 VR-150-30
V_3 VR-105-30
V_4 6SC7
V_5 IONIZATION GAUGE D.P.I., TYPE VG-1 OR EQUIVALENT
F 3-AMP FUSE
S_1 TOGGLE SWITCH
S_2 6-POINT TAP SWITCH
M_1 0-10 MA, D-C
M_2 0-5 ANP, A-C
M_3 0-50 μ ANP, D-C

Figure 3. Circuit Diagram of Ionization Gauge Power Supply and Amplifier.

heater manufactured by the Thermex Division of The Girdler Corporation, Louisville, Kentucky, was used. Because the unit was manufactured for dielectric heating, it was necessary to modify it in order to heat by induction. Induction heating was necessary with the adsorption material (charcoal) now under study since this material is a good electrical conductor. A two-inch-diameter coil of five turns of 1/4-inch copper tubing was used as the heating element. This coil was connected to the power supply in parallel with a large variable capacitor for balancing the external circuit. Efficient heating of the charcoal sample was obtained at a frequency of 15 megacycles and a voltage drop across the induction coil of about 1,000 volts. With this arrangement a charcoal sample could easily be heated to a temperature exceeding 1,200° C. Since the temperature of the sample was measured with an optical pyrometer, the temperature of the external portion of the sample was obtained, and since the center portion of the sample was hotter than the outer portion, the mean temperature of the sample has not been accurately determined. The portion of the apparatus containing the sample was constructed of Vycor glass in order that the sample might be heated to the high temperature.

A high temperature is necessary to free a solid surface of all adsorbed gases. Such a temperature, in the case of charcoal, is also sufficiently high to vaporize appreciable quantities of charcoal which then condense as graphite on cooler portions of the sample space. The formation of this graphite in the degassing process must be kept small if it is to have negligible effect on heat of adsorption results.

Figure 1 shows the induction heater in location for sample heating.

B. Procedure

The following procedure has been employed in obtaining adsorption data. One determination was made before induction heating was adopted for sample degassing, and three other determinations were made after induction heating was employed but before the removal of neon gas was attempted. Only preliminary tests have been made using the neon removal system. For that reason no results have been obtained yet using all of the improvements made. The various procedures outlined below are those which have been employed except that of neon removal. The procedure given for this case is that which probably will be followed in the future.

The sample to be used was first dried, weighed and placed into a sample tube exactly as has been done previously. The sample, in a Vycor sample tube, was then attached to the adsorption apparatus and evacuated to approximately 10 μ before induction heating was begun. Evacuation was continued while the sample was being heated to approximately 1,200° C. Heating was continued for about two hours. The last hour of this time the pressure usually remained about 5 μ. When the temperature was reduced to 900° C, the pressure dropped to about 0.1 μ. After evacuation, the sample tube stopcock was closed; the heater was removed; the sample was allowed to cool to room temperature; and liquid nitrogen baths were placed on the sample tube and on the vapor trap attached to the tube.

The helium and nitrogen purification systems were operated while the sealed-off sample was coming to temperature equilibrium. The copper powder column was filled with tank nitrogen and was electrically heated to approximately 300° C by means of resistance wire wound about the column. The charcoal traps were also heated electrically to about the same temperature and

were evacuated while being heated. After the traps were degassed at this condition, the heaters were turned off, and a liquid nitrogen bath was placed about the traps. Nitrogen was admitted from the copper column into one charcoal trap and helium was admitted into the other trap.

In future measurements, neon will be removed by fractional adsorption. After the nitrogen containing impurities has been adsorbed in the charcoal trap at the temperature of liquid nitrogen, the trap will be evacuated to a pressure of about 1,000 microns, removing most of the unadsorbed neon and other rare gases and, of course, part of the nitrogen. The liquid nitrogen will then be removed from the charcoal trap and placed on the condensation tube below the nitrogen reservoir, and the charcoal trap will be allowed to come to room temperature. Nitrogen desorbed by the charcoal will be condensed in the cold trap and if necessary, it will be readsorbed and recondensed. Then the purified nitrogen will be stored in the nitrogen reservoir.

The volume of the sample tube and the cold trap protecting the sample from mercury and other vapors was determined by expanding a known volume of helium into the sample space. Since the temperature of the tubing connecting the sample tube with the cold trap is not the same as that of the tube and trap, it is necessary to find an effective volume for the system at one temperature (liquid nitrogen temperature) in order to calculate the volume of gas adsorbed during the main part of the experiment. As derived in the last report, the volume of gas adsorbed with each increment of nitrogen added to the sample may be expressed by

$$V_a = \frac{273}{760}\left[\frac{V_t}{T_b}(p_1 - p_2) - \frac{V_s}{T_s'}(p_2 - p_o) - \alpha\frac{V_s}{T_s'}(p_2^2 - p_o^2)\right], \qquad (1)$$

where p_o = initial pressure in sample tube, mm. Hg,

p_1 = initial pressure in burette space, mm. Hg,

p_2 = final pressure in burette space and in sample tube, mm. Hg,

V_t = volume of burettes and connective tubing, ml.,

V_s = volume of sample tube and incorporated cold trap, ml.,

V_a = volume of gas adsorbed, cc. at S.T.P.,

T_b = temperature of burettes, ^oK,

T_s = temperature of sample space, ^oK,

T_s' = average temperature of sample space, incorporated cold trap and connective tubing, ^oK and

α = correction for deviation of nitrogen from perfect gas law = 6.6×10^{-5} (mm. Hg)$^{-1}$ at 78° K; and for oxygen, 3.8×10^{-5} (mm. Hg)$^{-1}$ at 90° K.

In order to determine the average temperature of the sample, T_s', it is first necessary to calibrate the volume of the sample tube, V_s, at room temperature. Using this value, the average temperature, T_s', may then be obtained after the sample has come to temperature equilibrium at liquid nitrogen temperature. It may be seen readily that an effective volume, V_s', could be used rather than an average temperature for calculating the volume of adsorbed gas. That is,

$$V_a = \frac{273}{760}\left[\frac{V_t}{T_b}(p_1 - p_2) - \frac{V_s'}{T_s}(p_2 - p_o) - \alpha\frac{V_s'}{T_s}(p_2^2 - p_o^2)\right] . \quad (2)$$

The effective volume of the sample tube assembly, V_s', may be determined in only one step. This method has the added advantage that the sample may be cooling while the gas to be adsorbed is being purified. Therefore, equation 2 was

used to calculate the volume of nitrogen adsorbed with each increment of gas after the effective volume of the sample was determined with helium.

After the volume of the sample space was determined, the helium was pumped from the system without removing the cold baths. After the entire system was evacuated to a pressure of 0.1 μ or less, the sample stopcock was closed and nitrogen was admitted to the system. An adsorption isotherm was determined in the usual manner except that longer periods than heretofore employed were allowed for equilibration before the equilibrium pressure, p_2, was recorded. This pressure was recorded only after no measurable change in pressure was observed in 30 minutes. This usually required two to three hours for the first few points and less than one hour for points at higher pressures.

C. Results

The adsorption data obtained by the methods outlined above are given in the Appendix. It will be noted that in the first run the sample was not evacuated at a high temperature. These data were obtained before the high-frequency induction heater was adapted for heating the sample. Even after the first system was added to the apparatus to remove impurities from the nitrogen gas, consistant results were not obtained. A hand spectrometer showed that neon, a noncondensable gas which would not be removed by the procedure employed, was present in the residual gas in the adsorption space. The presence of this gas, even in very small amounts, invalidated the equilibrium pressure measurements as may be seen by the data given. Adsorption data have not been obtained using the latest gas purification system.

IV. DISCUSSION OF RESULTS

A. Apparatus

1. Gas Purification

The purification of helium by passage over degassed charcoal at liquid nitrogen temperature is apparently satisfactory. Similar systems have also been used by Harris and Emmett[3] and by Beebe, Millard and Cynarski[4] with equal success.

The purification of the nitrogen was not successfully accomplished as first attempted. Since nitrogen gas is obtained by the fractional distillation of liquid air, small quantities of the gases found in air are retained as impurities. Of these gases, probably almost all of the oxygen and hydrogen are removed in the copper column and carbon dioxide in the charcoal trap. However, little of the argon or krypton and practically no neon or helium are removed in either system. In fact, since a large volume of nitrogen is adsorbed by the charcoal and little neon or helium is adsorbed, the concentration of inert gases in the nitrogen passing through the charcoal is actually increased rather than decreased. Therefore, the first increments of gas added to the sample contained more of the inert gases than later increments contained after the charcoal was saturated with nitrogen. A comparison of the spectrum of the residual gases in the adsorption system with the spectrum of neon indicated that relatively large quantities of this gas were present. Although the neon present was sufficient to invalidate equilibrium pressure measurements in the micron pressure range, one calculation showed

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[3] Harris, B. L., and Emmett, P. H., "Physical Adsorption of Toluene, Benzene, Ethyl Iodide, Hydrogen Sulfide, Water Vapor, Carbon Disulfide, and Pentane on Various Porous and Non-Porous Solids." J. Phys. and Colloid Chem. 53, 811-25 (1949).

[4] Beebe, R. A., Millard, B., and Cynarski, J., Op. cit.

that not more than 0.25 per cent neon was present in the initial increment of gas. This emphasizes the importance of obtaining nitrogen as pure as possible.

The second system employed for the purification of nitrogen utilized essentially the same components as the first, but the procedure employed was designed to remove the rare gases rather than to concentrate them. The system has been satisfactory insofar as it has been tested.

2. Pressure Measurement

Three devices have been provided with which to measure pressure for the entire pressure range of interest in this work. Each device functions best over a limited range, but the ranges overlap sufficiently for the devices to be checked against each other. These checks and other pressure measurements with the devices have been quite satisfactory.

3. Sample Preparation

The use of the high-frequency induction heater for sample degassing not only greatly reduces the time necessary for removing gases but it also ensures that more complete degassing can be accomplished. The main question involved in the use of high temperatures for degassing is sample alteration. For charcoal, the allowable temperature seems to be quite high, and high temperature seems to provide the most satisfactory means of degassing yet found.

B. Procedure

The procedure for determining the volume of the sample space has been satisfactory in all respects since the helium has been purified as described. The procedure for removing neon from the nitrogen has not been completely tested to determine its effectiveness, but it is known to result in much

purer nitrogen than was previously available. The procedure for measuring the volume of gas adsorbed has been thoroughly tested and is entirely satisfactory.

C. Results

It may be seen from the data in the Appendix that the equilibrium results were not sufficiently consistent to calculate heats of adsorption. On the last run, the adsorption space, exclusive of the sample space, was evacuated after each run. When this was done, the equilibrium pressure decreased for five successive points before it began to increase again. No quantitative measurements were made; however, the indication was that the amount of neon present in the residual gas decreased with each increment of gas. The errors in the data revealed by these experiments were present in some degree in all previous data.

V. FUTURE WORK

All efforts during the remainder of this contract will be directed toward making adsorption measurements and calculating heats of adsorption from the resulting data. It is believed that the primary problems involved in sample preparation, gas purification and pressure measurement have been overcome, and that prospects for accomplishing heat of adsorption measurements are good.

Several problems remain which may require solution, however. The two of most concern at the present involve regulation of the adsorption space temperature at several temperatures between the normal boiling points of liquid nitrogen and liquid oxygen, and the fact that at least one ground glass stopcock of the many stopcocks used in the current apparatus is almost always leaking enough to give trouble. Since it is possible to regulate the sample space temperature to within approximately 0.1° K simply by preparing a mixture

of liquid nitrogen and liquid oxygen and by carefully adding one component as necessary, the first problem does not appear to be pressing. The second problem can be solved only by eliminating glass stopcocks. All-metal vacuum systems have been used quite satisfactorily in comparable research. However, construction of such a system during the time remaining for the present contract is impossible.

VI. PERSONNEL

The technical personnel who worked on this project and the percentage of working time each devoted to the project during the period covered by this report are shown below. Mr. M. T. Gordon, a research chemical engineer of the Engineering Experiment Station, who has had considerable experience in electronics, helped set up the ionization gauge, the high voltage source for degassing the gauge and the induction heater for sample degassing. Miss Jane Barrett became Mrs. Jane B. Garrett on December 27, 1953.

Name	Title	Percentage of Working Time Devoted to Project
Clyde Orr, Jr.	Project Director	50
H. G. Blocker	Research Engineer	100
M. T. Gordon	Research Engineer	20
Mrs. Jane B. Garrett	Research Assistant	30

Respectfully submitted:

Clyde Orr, Jr.

Clyde Orr, Jr.,
Project Director

H. G. Blocker

H. G. Blocker,
Research Engineer

Jane B. Garrett

Jane B. Garrett,
Research Assistant

Approved:

Herschel H. Cudd

Herschel H. Cudd, Director
Engineering Experiment Station

VII. APPENDIX

TABLE I

EXPERIMENTAL NITROGEN GAS ADSORPTION DATA

p_1 (mm. Hg)	p (mm. Hg)	V (cc./g.)	Constants*
1. Coconut Charcoal:**			
145.7	0.0093	10.74	w = 1.9005 g.
147.6	0.0110	21.63	T_b = 300.1° K, 299° K
159.0	0.039	33.36	T_s = 77.8° K,
166.7	0.138	45.65	77.7° K
165.4	0.192	57.84	V_s = 20.0 cc.
			V_t = 117.1 cc.
2. Coconut Charcoal:			
101.9	0.0031	7.54	w = 1.9005 g.
108.5	0.0112	15.57	T_b = 299° K
299.8	0.030	32.59	T_s = 89.73° K
224.9	0.055	49.24	V_s = 20.6 cc.
226.9	0.275	66.03	V_t = 117.1 cc.
251.4	0.38	84.64	
247.9	0.53	102.99	
279.4	0.85	123.66	
280.6	1.62	144.29	
316.8	3.80	167.37	
333.8	10.98	190.95	
357.3	33.44	213.96	
367.5	78.85	233.35	
394.4	144.1	249.02	
3. Coconut Charcoal:			
204.2	0.0030	5.07	w = 5.6096 g.
241.0	0.0065	11.05	T_b = 302° K, 299.6° K
245.7	0.0132	17.16	T_s = 78.2° K
264.2	0.0150	23.78	V_s = 38.86 cc.
297.0	0.0170	31.21	V_t = 117.1 cc.
318.5	0.0190	39.19	

(Continued)

TABLE I (Continued)

EXPERIMENTAL NITROGEN GAS ADSORPTION DATA

P_1 (mm. Hg)	p (mm. Hg)	V (cc./g.)	Constants*
4. Coconut Charcoal:			
274.9	0.0181	12.74	w = 5.6096 g.
362.9	0.102	29.56	T_b = 299.6° K
373.5	0.100	46.88	T_s = 78.8° K
368.0	0.075	63.94	V_s = 38.9 cc.
478.7	0.081	86.13	V_t = 217.1 cc.
500.8	0.059	109.35	
522.5	0.060	133.57	
520.6	0.104	157.70	
522.4	0.265	181.90	
537.2	0.870	206.77	
542.0	3.48	231.65	
557.1	12.64	256.60	

* When more than one value is given for a constant, the first value refers to the first group of data and the second to the second group.

** Description of pretreatments:

1. Evacuated 16 hrs. at 300° C to 0.1 μ pressure.
2. Evacuated 2 hrs. at 1,200° C to 5 μ pressure.
3. Evacuated 2 hrs. at 1,200° C to 5 μ pressure; 900° C to 0.1 μ pressure.
4. Evacuated 2 hrs. at 1,200° C to 0.2 μ pressure.

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APRIL 30, 1954

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I. ABSTRACT

The general purpose of this investigation and of those which preceded it was an evaluation of the surface properties of finely divided solid materials. This particular project was concerned with heats of adsorption, i.e., the heat released at a solid's surface upon contact with a gas.

Two independent methods were used in making heat of adsorption measurements. Experimental data were obtained for a nickel-silica catalyst, powdered nickel and coconut charcoal. Considerable attention was given to gas purification, to solid surface preparation and to pressure measurements in the low-pressure range.

Most extensive investigation was given to the charcoal. For this material, it was found that the first molecules of nitrogen gas adsorbed gave up considerably more energy than condensation released, and that later adsorbing molecules gave up only a little more energy than is released by the process of condensation, while still later adsorbing molecules gave up approximately twice the heat of condensation until complete monolayer coverage of the solid's surface resulted. The other materials gave similar results in the range of conditions in which they were investigated.

Since other investigators have obtained widely differing results, and since minor impurities are thought to alter the results obtained to a very great degree, future research in the field must give extensive consideration to impurities.

II. PURPOSE

An evaluation of the surface properties of finely divided solid materials so that the standardization of these properties may be attained is one ultimate goal of much current research. In this investigation, the heat of adsorption, i.e., the heat liberated when a gas is adsorbed on the surface of a powdered solid, has been studied.

Heat of adsorption is of both theoretical and practical importance, it being indicative of the energy states of atoms in surface layers. The surface atoms of clean solids are subjected to unbalanced forces due to the presence of other atoms in one direction only. Consequently, when a gas is brought into contact with the fresh surface of a solid, some of the gas molecules become attached to the solid thus satisfying this unbalance of forces and releasing a quantity of energy as heat, the amount of which depends on the state of attachment. Much is to be learned from heat of adsorption measurements about the structure of solid surfaces, about the properties of catalysts in regard to particular chemical reactions under certain conditions, about chemisorption, about physical adsorption and about other properties.

Because of the small quantities of heat which must be measured, relatively few measurements have been made by investigators. This research was undertaken to supply additional data.

III. EXPERIMENTAL WORK

A. Apparatus

1. Isothermal Calorimeter

An isothermal calorimeter was used to measure directly the heat liberated by the adsorption of gas molecules on the surface of a clean solid. This

apparatus was constructed in such a manner as to use the vacuum- and pressure-measuring facilities of the adsorption apparatus used in work under a previous contract[1]. A schematic diagram of this calorimeter is given in Figure 1.

The entire calorimeter proper was immersed in liquid nitrogen to ensure a constant temperature throughout the sample before adsorption was begun. In the apparatus, the heat liberated upon adsorption resulted in the vaporization of some of the liquid nitrogen in the chamber surrounding the sample. Vaporization was made to occur at constant pressure by means of a solenoid-operated valve which was, in turn, activated by contacts located in the pressure manometer. The calorimeter was constructed of Pyrex glass with the exception of the sample tube itself, which was made of Vycor glass in order to withstand higher temperatures for more thorough sample degassing. The thickness of the wall of this sample tube was reduced by controlled etching with hydrofluoric acid to about 0.2 mm. Etching was limited to the outside of the tube so that a smooth surface would be maintained on the inner surface, where adsorption would occur. The thin wall was desirable because it permitted a more rapid heat transfer between the sample and the liquid nitrogen surrounding the sample tube, and, also, because it reduced heat transfer along the wall in a direction perpendicular to the desired direction of flow. The functioning of the apparatus and the procedure for making a heat of adsorption determination are described in a later section.

2. Isosteric System

A second adsorption apparatus was constructed and subsequently altered in order to obtain more accurate adsorption isotherms from which heats of

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[1] DallaValle, J. M., Orr, C., Jr., and Blocker, H. G., Research on Surface Properties of Fine Particles. Final Report, Project 181-119, Contract No. DA-36-039-sc-5411, Georgia Institute of Technology, Atlanta, Georgia, April 30, 1953.

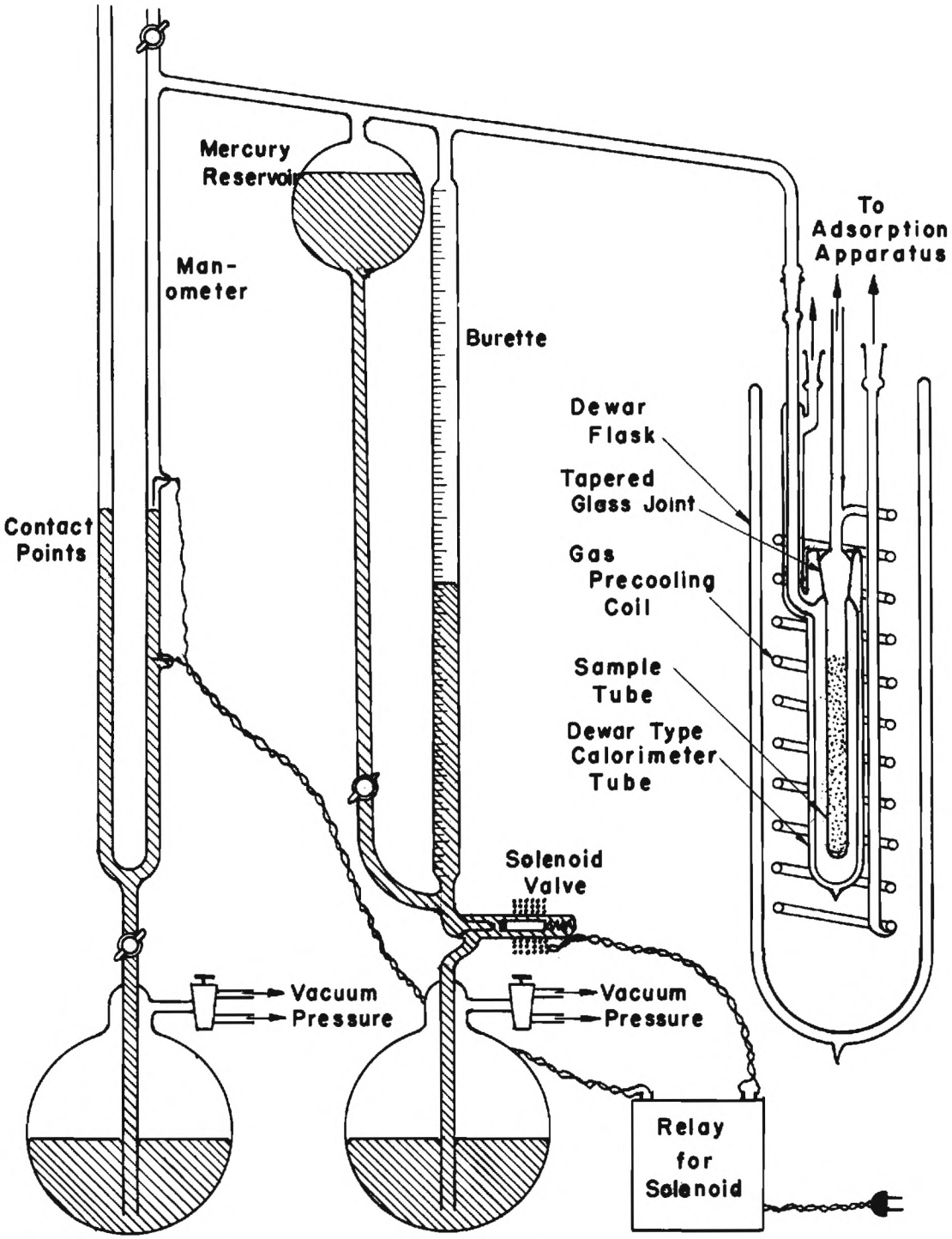


Figure 1. Schematic Diagram of Isothermal Calorimeter.

adsorption could be calculated. The new adsorption apparatus was constructed primarily of Pyrex glass, using standard-taper stopcocks with interchangeable plugs. Some of the difficulty encountered due to leaking stopcocks was eliminated by lapping them with No. 400 and No. 600 silicon carbide grit.

Special features of the apparatus are described below. A schematic drawing of the apparatus is given in Figure 2. Figure 3 is a photograph of the apparatus in operation.

a. Induction Heater. In the early part of this investigation, Glas-Col heating mantles were used to heat the samples during the degassing period. Sample temperatures up to 350° C could be maintained with this arrangement. Later an induction heater was set up for more thorough degassing of the adsorption sample than was formerly possible. For this purpose a Model 2 dielectric heater manufactured by the Thermex Division of the Girdler Corporation, Louisville, Kentucky, was used. Because the unit was manufactured for dielectric heating, it was necessary to modify it in order to heat by induction. A two-inch-diameter coil of five turns of 1/4-inch copper tubing was used as the heating element. This coil was connected to the power supply in parallel with a large variable capacitor for balancing the external circuit. Satisfactory heating of the charcoal sample was obtained at a frequency of 15 megacycles and a voltage drop across the induction coil of about 1,000 volts. With this arrangement a charcoal sample could easily be heated to a temperature exceeding 1,200° C, as measured with an optical pyrometer. The portion of the apparatus containing the sample was constructed of Vycor glass in order to withstand this temperature.

Figure 3 shows the induction heater in location for sample heating.

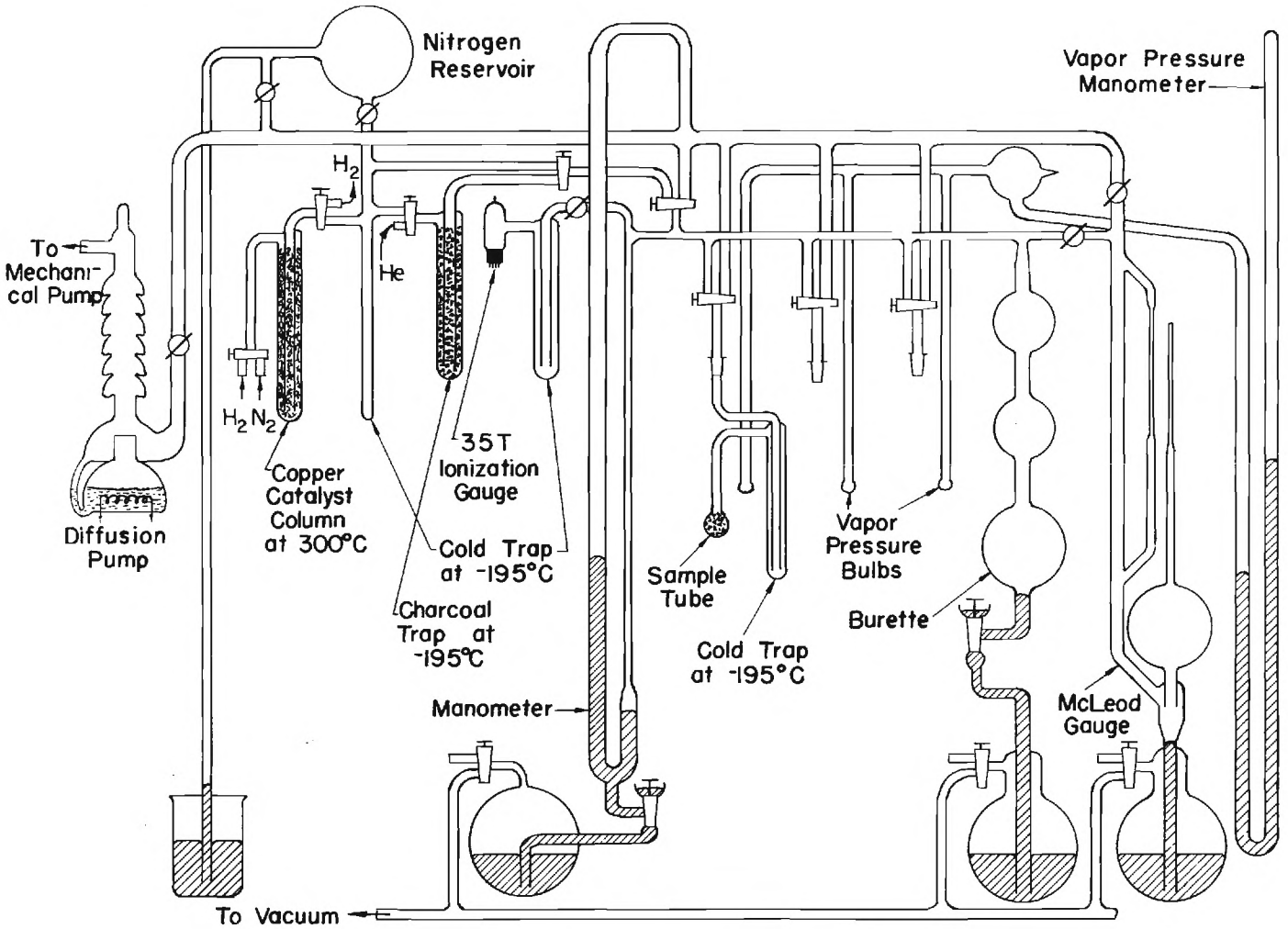


Figure 2. Schematic Diagram of Heat of Adsorption Apparatus.

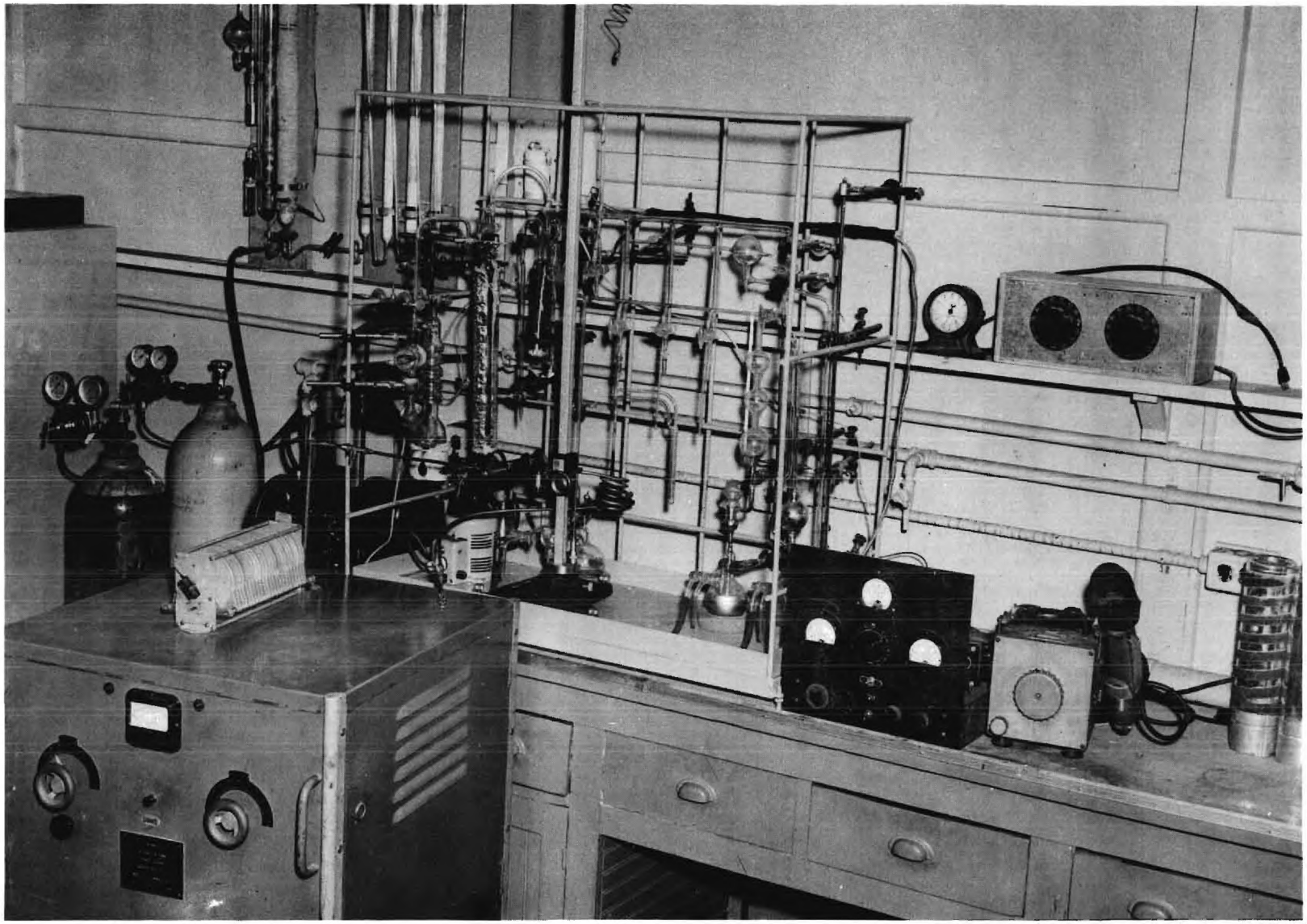


Figure 3. Heat of Adsorption Apparatus.

b. Pressure-Measurement Instruments. Measuring the pressures encountered at low-surface coverage caused difficulty in obtaining accurate adsorption data during the early portions of this investigation. Devices finally were made which enabled pressure measurements to be taken with precision over a wide range of pressures.

A mercury manometer, constructed of 15-mm. internal-diameter Pyrex tubing, was used to measure pressures in the range one to 800 mm. Hg. This large-diameter tubing was used to minimize capillarity effects and to reduce the error caused by the adhesion of mercury to the manometer walls. A cathetometer was used to obtain the difference in the heights of the mercury columns in the manometer. This cathetometer had a twenty-power telescope which rotated about a vertical axis and could be focused on the top of the meniscus in either leg of the manometer. The height of the mercury was measured with a vernier scale which could be read directly to 0.1 mm. over the range 0 to 800 mm. For more accurate measurement of pressures up to 100 mm. Hg, the height of the telescope above the base of the cathetometer was measured with a micrometer to within 0.0005 inch or approximately 0.01 mm.

Pressures between 10^{-5} and one mm. Hg were measured with a double-range McLeod gauge. A 0.5-mm.-diameter capillary tube was sealed to the upper end of a 2.5-mm.-diameter capillary tube (see Figure 2) in order to extend the pressure range over which accurate measurements could be made with this instrument.

An ionization gauge was installed to extend the range in which accurate pressure measurements could be made down to approximately 10^{-6} mm. Hg. Continuous pressure measurements could be obtained from this pressure up to about 5×10^{-3} mm. Hg. The gauge, an Eitel-McCullough, Inc., San Bruno, California,

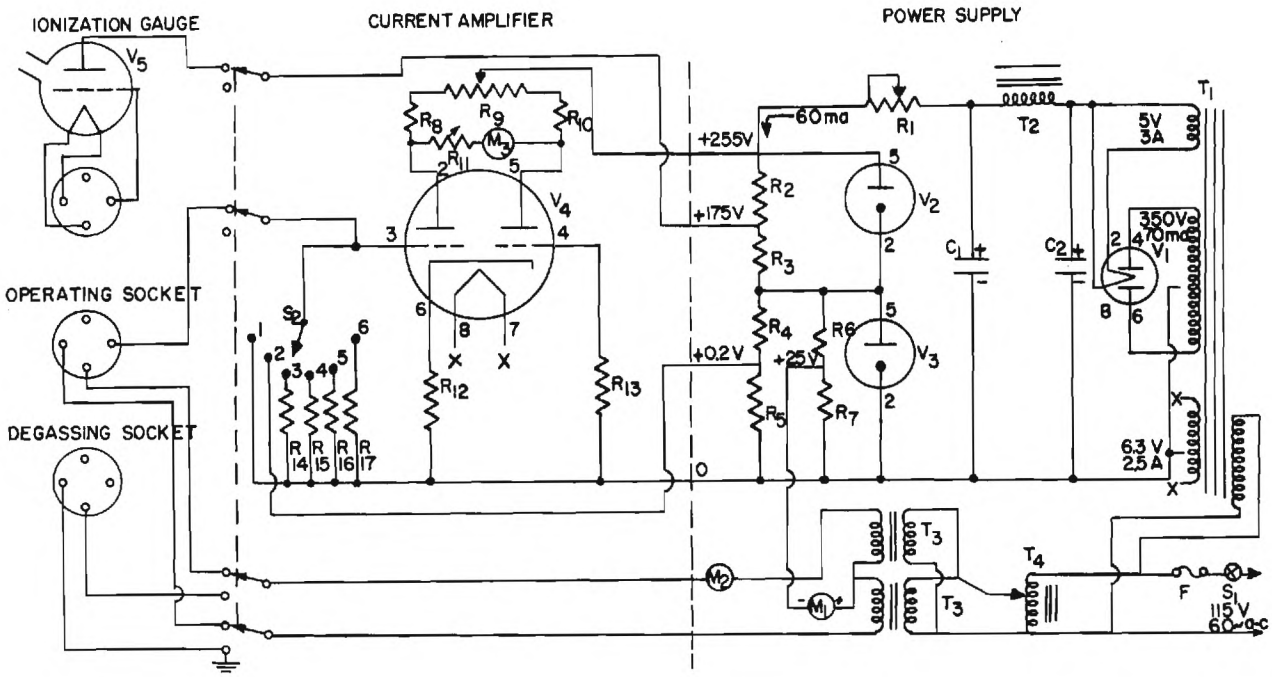
type 35T tube, was connected to the adsorption space through a stopcock and a cold trap filled with liquid nitrogen to protect the tube from mercury vapor. The circuit diagram of the power supply and amplifier for this gauge is shown in Figure 4.

Degassing the ionization gauge was accomplished by applying 1,500 volts dc from an external source to the plate of the ionization gauge and increasing the filament voltage until the plate became cherry red. Provisions were made for grounding the filament and disconnecting the grid during degassing. The tube was evacuated to a pressure of about 0.2 micron while being heated.

c. Gas-Purification System. Very small changes in the pressure or in the quantity of gas adsorbed are important when measuring heats of adsorption, hence, impurities must be removed if accurate heat of adsorption data are to be obtained. Therefore, the gas purification system shown with the apparatus in Figure 2 was incorporated in order to increase the purity of the adsorbing gas and, thereby, to increase the accuracy of adsorption measurements.

A column containing powdered copper was employed to remove oxygen from the nitrogen. Minus 100-mesh powder was compressed into minus 20- to plus 80-mesh aggregates before it was placed in the column so that the gas could flow through the bed easily. The powder was reduced with hydrogen at about 300° C before use; it was maintained at this same temperature during use for oxygen removal.

Some of the rare gases were found to be present in the nitrogen being used in sufficient quantities to invalidate many pressure measurements in the low-pressure region. These gases were removed by selective adsorption. A charcoal-filled cold trap, a condensation tube and a five-liter gas-storage flask with a mercury manometer for indicating pressure were interconnected, as shown in



C_1 30 μfd ELECTROLYTIC, 450 VOLTS
C_2 30 μfd ELECTROLYTIC, 450 VOLTS
R_1 3,000 OHMS, 5 WATTS
R_2 2,250 OHMS, 5 WATTS
R_3 2,500 OHMS, 2 WATTS
R_4 4,000 OHMS, 2 WATTS
R_5 950 OHMS, 2 WATTS
R_6 20,000 OHMS, 2 WATTS
R_7 38 OHMS, 2 WATTS
R_8 10,000 OHMS, 2 WATTS
R_9 5,000 OHMS, 4 WATTS
R_{10} 10,000 OHMS, 2 WATTS
R_{11} 25,000 OHMS, 4 WATTS, WIRE-WOUND
R_{12} 2,000 OHMS, 2 WATTS
R_{13} 2 MEGOHMS, 1 WATT
R_{14} 2,000 OHMS, 1 WATT, WIRE-WOUND PRECISION
R_{15} 20,000 OHMS, 1 WATT, WIRE-WOUND PRECISION
R_{16} 200,000 OHMS, 1 WATT, WIRE-WOUND PRECISION
R_{17} 2 MEGOHMS, 2 WATTS, WIRE-WOUND PRECISION

T_1 POWER TRANSFORMER (THORDARSON T-13R12 OR EQUIVALENT)
T_2 CHOKE, 10H, 110 MA (THORDARSON T-57054 OR EQUIVALENT)
T_3 FILAMENT TRANSFORMER, 5 VOLTS, 4 AMPS (THORDARSON T-63F99 OR EQUIVALENT)
T_4 1-AMP VARIAC, TYPE 200-B
V_1 5U4-G
V_2 VR-150-30
V_3 VR-105-30
V_4 6SC7
V_5 IONIZATION GAUGE D.P.I., TYPE VG-1 OR EQUIVALENT
F 3-AMP FUSE
S_1 TOGGLE SWITCH
S_2 6-POINT TAP SWITCH
M_1 0-10 MA, D-C
M_2 0-5 ANP, A-C
M_3 0-50 μ ANP, D-C

Figure 4. Circuit Diagram of Ionization Gauge Power Supply and Amplifier.

Figure 2, so that each component could be evacuated separately. Resistance wire was cemented onto the charcoal trap and served to heat the charcoal adsorbent when it was being evacuated and prepared for use. The procedure for purifying the gas will be described in a later section.

In addition to impurities in the nitrogen gas admitted into the system other impurities were guarded against also. All of the mercury in the system was removed, the system was thoroughly cleaned and the mercury was triple distilled before it was replaced in the apparatus.

A cold trap maintained at liquid-nitrogen temperature was installed between the sample and the rest of the system in order to prevent mercury, stopcock grease and other vapors from reaching the sample.

d. Temperature Regulation. One of the problems involved in determining adsorption isotherms was control of the adsorption-space temperature. The difficulty was not in measuring the temperature but in controlling it at several levels. The temperature of the adsorption space was measured with an argon vapor pressure thermometer.

It was possible to control the temperature of the sample within approximately 0.1° K variation by preparing a mixture of liquid nitrogen and liquid oxygen and by adding carefully one component or the other to the space about the sample as necessary to maintain a certain liquid level and to maintain the desired temperature.

B. Procedure

1. Isothermal Calorimeter

The calorimeter was checked by replacing the sample with a small resistor, passing a known current through the resistor, measuring the heat

released and comparing this heat with that calculated from the current employed. The results of several such tests indicated that nearly all of the heat added to the system was used to vaporize the liquid surrounding the sample.

a. Sample Preparation. Most of the heat of adsorption measurements made using this apparatus were determined on coconut charcoal. Prior to these measurements, the material was cleaned as follows:

(1) The charcoal was washed with a 10 per cent nitric acid solution, the acid was decanted and the charcoal was rinsed twice with distilled water.

(2) The charcoal was washed with a 10 per cent hydrochloric acid solution and rinsed as before.

(3) The charcoal was washed with a 1/100 N sodium hydroxide solution and rinsed as before.

(4) The charcoal was refluxed with a 20 per cent solution of hydrochloric acid in a Soxhlet extractor for one and one-half hours.

(5) The charcoal was rinsed several times with distilled water and was then refluxed with water in the extractor using several changes of water until a sodium-flame test of the water in the flask was negative.

(6) The charcoal was dried.

One determination in the early part of this investigation was made with a high-surface-area nickel silica catalyst supplied by the Girdler Corporation, Louisville, Kentucky. This material, designated G-12, was originally prepared in the form of pellets approximately one-quarter inch in diameter. To increase the rate of adsorption, the pellets were crushed and the fraction minus 12- and plus 20-mesh was retained for the measurements.

All samples were dried, weighed and placed in a calorimeter sample tube before being attached to the apparatus. Next, the tube extending from the top of the calorimeter was welded to an extension leading directly to the high-vacuum manifold at the top of the apparatus. Then evacuation was begun. The samples were heated to approximately 350° C by means of an electric-resistance heater while being evacuated to a pressure near 0.1 micron. After prolonged degassing (18 to 20 hrs.), the tube leading to the top of the calorimeter was sealed off and the sample was permitted to cool.

b. Calorimetric Measurements. The calorimeter evaporation chamber was filled with liquid nitrogen and was then attached inside the cooling coil in such a manner that the coil surrounded the sample tube. The calorimeter evaporation chamber was attached to a burette as well as to the sample tube. Care was taken to fill the evaporation chamber with enough liquid nitrogen to ensure the sample's being completely below the liquid level. The entire calorimeter was finally immersed in another liquid-nitrogen bath.

With the mercury level in the upper portion of the burette which was joined to the solenoid valve, the pressure controller was adjusted so that, after the sample, bath and calorimeter evaporation chamber had come to the same temperature, the level of the mercury in the burette changed very slowly with time. When properly adjusted, such change as occurred was brought about by the slight amount of heat leaking into the system. If the composition of the liquid in the calorimeter and in the outer bath were identical, the levels of the mercury columns in the pressure controller would be equal. Since the outer bath was exposed to the atmosphere, the liquid nitrogen could not be completely prevented from absorbing oxygen from the air and this condition was not quite

attained. A measured amount of gas was then slowly admitted to the sample tube. The coil about the calorimeter tube served to cool the gas to the temperature of liquid nitrogen before it entered the sample tube to be adsorbed. The heat liberated during adsorption was conducted through the sample-tube walls into the liquid nitrogen in the calorimeter evaporation chamber. The liberated heat evaporated some of the liquid in the calorimeter tube and tended to cause an increase in gas pressure. As a slight pressure was developed, however, the pressure controller activated the solenoid valve lowering the mercury level in the burette and reducing the pressure to its original value. Thus, evaporation was made to occur at an essentially constant pressure. Other increments of gas were admitted after the first increment was completely adsorbed, and the procedure was repeated for each increment.

A mercury reservoir was connected through a stopcock to the burette to permit continuation of a determination if the volume of nitrogen evaporated was more than sufficient to replace all of the mercury in the burette.

The quantity of gas resulting from the evaporation due to each gas addition was then determined from the volume of the burette space and the temperature and pressure of the gas.

2. Isostere Determination

Isotherms from which heats of adsorption were calculated were obtained with nitrogen gas and the specially prepared coconut charcoal described in a previous section. Isotherms were also obtained with nitrogen gas and a specially prepared high-surface nickel adsorbent. The preparation of this adsorbent is described on the following page.

a. Sample Preparation. Nickel of colloidal dimensions was prepared using a high-surface sodium technique[2]. The apparatus employed for this preparation was designed so that the sodium could be prepared and then used to produce the nickel in a single reaction vessel. A three-necked flask was used as the vessel. Through the center opening entered a pivoted, semicircular, glass stirring blade connected by a glass rod to a motor. A mercury-seal bearing prevented gas leaks. One of the side openings of the three-necked flask was used for the introduction of reactants. The third opening in the reaction vessel was equipped with a gas lock and was used for the addition of sodium. A rubber hose attached to this opening was opened and closed with a pinchclamp, which allowed the sodium to be kept in an inert atmosphere of nitrogen before and during addition into the reaction vessel. The reaction vessel was encased by a heating mantle and was provided with a thermocouple with which its temperature was determined.

The nickel preparation was accomplished as follows: The air in the reaction vessel was displaced by nitrogen, and this inert atmosphere was then maintained throughout the process by continuously admitting and venting more of the gas. Sodium chloride was employed as the inert carrier for the high-surface sodium, and 144 grams of dry sodium chloride were placed in the reaction flask through the addition tube. The temperature of the flask was raised to 150°-200° C, and approximately 2.5 grams of sodium were added. The sodium was dispersed on the surface of the salt by vigorous mixing of the sodium and the salt. After the sodium was dispersed and while the stirring continued, 10 grams of dried and finely powdered nickel chloride were added slowly. The

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[2] U. S. Industrial Chemicals Co., High Surface Sodium on Inert Solids. New York, 1953.

if it is to have a negligible effect on the heat of adsorption results. Therefore, the heating period was kept as small as possible.

b. Gas Purification. Nitrogen gas to be adsorbed was purified and stored in the large flask provided for this purpose. The following procedure was employed in purifying the nitrogen: The entire purification system, consisting of the storage vessel, adsorbent and reaction columns, connecting tubing, etc., was evacuated to a pressure of about 0.1 micron while the charcoal trap and gas reservoir were then closed off and the charcoal trap was cooled to liquid-nitrogen temperature. The copper-powder column was filled with nitrogen which was slowly admitted into the system through the charcoal trap. Most of the nitrogen was readily adsorbed on the charcoal while unadsorbed neon and other gases passed through the trap and were removed from the system by the vacuum pump. When the pressure of the gas in the adsorption system rose to about one mm. Hg, the charcoal trap was closed off and the flow of nitrogen was stopped. The condensation tube was then evacuated, cooled to liquid-nitrogen temperature and opened to the charcoal trap. The liquid-nitrogen bath was removed from the charcoal trap, and, as the charcoal warmed to room temperature, the desorbing nitrogen was collected in the condensation tube by surrounding the tube with liquid nitrogen. The collected nitrogen was then distilled at liquid-nitrogen temperature, and the first three-fourths was collected in the gas reservoir.

The small amounts of impurities in the helium were removed by passing this gas into the adsorption system through the degassed-charcoal trap maintained at liquid-nitrogen temperature. No reservoir was used for the helium.

c. Isotherm Determination. After the surface of the sample had been cleaned and pure gas for adsorption had been prepared, the following procedure was employed in obtaining adsorption data: Since the sample tube, the cold trap protecting the sample from foreign vapors and the connecting tubing were not at the same temperature, it was necessary to determine an effective volume for this space at the temperature of the cold bath in order to calculate the volume of gas adsorbed at higher pressures. This was accomplished by expanding a known volume of helium into the sample space. On succeeding runs with the same sample, it was unnecessary to recalibrate the volume, and this step was omitted.

After the volume of the sample space was determined, the helium was pumped from the sample space and the entire system was evacuated to a pressure of less than 0.1 micron. The sample stopcock was then closed, the mercury was raised in the manometer and purified-nitrogen gas was led into the burette space. The pressure, temperature and volume of this gas was noted and it was expanded into the sample tube. After pressure equilibrium was reached the pressure was recorded and a second increment of gas was admitted to the sample, the process being repeated until sufficient data for the required measurements were obtained.

Equilibrium pressures of less than one mm. Hg were measured with the McLeod or ionization gauge; higher pressures were measured with the manometer. For the nickel, equilibrium pressure was attained in about 30 minutes for the first point and 10 to 20 minutes for other points. With charcoal, equilibrium was not attained for several hours, and the pressure was not recorded until no pressure change was observed for at least 30 minutes.

C. Calculations

1. Heats of Adsorption from Calorimetric Measurements

Heats of adsorption obtained with the constant-temperature calorimeter were determined from the latent heat of vaporization of the calorimetric medium, a mixture of liquid nitrogen and liquid oxygen, and the volume of evaporated gas. The heat liberated, H_a, with each increment of gas added to the sample, in calories, is

$$H_a = \frac{H_v V_v}{22,400} \times \frac{760}{p_b} \times \frac{T_b}{273} , \qquad (1)$$

where H_v = heat of vaporization of calorimetric medium, cal./mole,

p_b = pressure of gas in calorimeter burette, mm. Hg,

T_b = temperature of gas in burette, ^oK

and V_v = volume of gas evaporated in calorimeter, cc.

In order to obtain the average differential heat of adsorption for each increment, H_a for that increment must be divided by the number of moles of gas adsorbed by the sample during the increment in which the heat liberated was H_a, i.e.,

$$H_d = 22,400 \frac{H_a}{V_a} , \qquad (2)$$

where H_d = differential heat of adsorption, cal./mole

and V_a = volume of gas adsorbed, cc. at S.T.P.

The volume of gas adsorbed during each calorimetric measurement, V_a, was determined as follows: The quantity of gas in any section of the system is a function of pV/T. On successive adsorptions, the initial pressure in the sample tube will be the same as the previous equilibrium pressure, since the sample stopcock was closed after the previous equilibrium pressure was measured. A

material balance on the quantity of gas in the system before and after this stopcock is opened results in the equation

$$\frac{p_1 V_t}{T_b} + \frac{p_o V_s}{T_s}(1 + \alpha p_o) = \frac{pV_t}{T_b} + \frac{pV_s}{T_s}(1 + \alpha p) + \frac{760 V_a}{273}, \qquad (3)$$

where V_t = volume of burette space and connective tubing, cc.,

V_s = effective volume of the sample tube and connective tubing, cc.,

V_a = volume of gas adsorbed by sample, cc. at S.T.P.,

T_b = temperature of V_t, °K,

T_s = temperature of V_s, °K,

p_o = initial pressure of gas in V_s, mm. Hg,

p_1 = initial pressure of gas in V_t, mm. Hg,

p = equilibrium pressure of gas, mm. Hg

and α = factor to correct for deviation of gas from perfect gas law = 6.6×10^{-5} (mm. Hg)$^{-1}$ for nitrogen at 78° K.

This equation may be solved for V_a, the volume of gas adsorbed at standard conditions of temperature and pressure, giving

$$V_a = \frac{273}{760}\left[\frac{V_t}{T_b}(p_1 - p) - \frac{V_s}{T_s}(p - p_o) - \frac{V_s}{T_s}\alpha(p^2 - p_o^2)\right]. \qquad (4)$$

Isotherms of different materials may be more readily compared if the volume of gas adsorbed is reduced to a weight basis by dividing by the weight of sample, w. Then

$$\frac{V_a}{w} = \frac{273}{760w}\left[\frac{V_t}{T_b}(p_1 - p) - \frac{V_s}{T_s}(p - p_o) - \frac{V_s}{T_s}\alpha(p^2 - p_o^2)\right], \qquad (5)$$

gives the volume of gas adsorbed per unit weight of sample for each increment of gas. The total volume of gas adsorbed per unit weight of sample after each increment of gas, V, is the summation of the terms V_a/w. The adsorption isotherm is obtained by plotting p versus V.

Liquid nitrogen was used as the calorimetric medium throughout this part of the investigation. However, since this nitrogen contained a small, variable amount of liquid oxygen, it was necessary to evaluate the heat of vaporization for this mixture. Only limited heat of vaporization data could be found in the region of interest, and it was necessary to calculate the required information from other thermodynamic properties using such data as were available.

The assumptions made in order to carry out these calculations were (1) a mixture of liquid oxygen and liquid nitrogen is an ideal solution, (2) the vapor phase is an ideal solution, (3) the vapor and liquid phases were in equilibrium, (4) the specific volume of the vapor phase may be found by using a generalized compressibility factor and (5) the change in specific volume due to evaporation is proportional to the specific volume of the vapor.

Calculations were based on the thermodynamic relationship

$$H_v = y_n H_n + y_o H_o \qquad (6)$$

where H_v = heat of vaporization of the oxygen-nitrogen mixture, cal./mole,

H_o = heat of vaporization of the oxygen, cal./mole,

H_n = heat of vaporization of the nitrogen, cal./mole,

y_o = mole fraction of oxygen in the vapor phase

and y_n = mole fraction of nitrogen in the vapor phase.

The heats of vaporization of oxygen and nitrogen were obtained from the Clapeyron-Clausius equations for these gases,

$$H_o = T \Delta V_o \frac{dp_o}{dT} \qquad (7)$$

and

$$H_n = T \Delta V_n \frac{dp_n}{dT} \quad , \qquad (8)$$

where T = temperature, °K,

ΔV_o = change in volume due to evaporization of oxygen, cal./mole, mm. Hg,

ΔV_n = change in volume due to evaporization of nitrogen, cal./mole, mm. Hg,

p_o = vapor pressure of oxygen, mm. Hg

and p_n = vapor pressure of nitrogen, mm. Hg.

The derivatives dp_o/dT and dp_n/dT were determined from the vapor pressure-temperature relationships for oxygen and nitrogen given by Farkas and Melville[3] which are, respectively,

$$\log p_o = -\frac{419.30}{T} + 8.1173 - 0.0648T \qquad (9)$$

and

$$\log p_n = -\frac{334.64}{T} + 7.5778 - 0.00476T \quad . \qquad (10)$$

The specific volumes of the vapor phases were obtained from the equations

$$V_o = \frac{ZRT}{p_o} \qquad (11)$$

and

$$V_n = \frac{ZRT}{p_n} \quad , \qquad (12)$$

where V_o = specific volume of the oxygen, cal./mole, mm. Hg,

V_n = specific volume of the nitrogen, cal./mole, mm. Hg,

R = the gas constant, cal./mole, °K

and Z = generalized compressibility factor[4].

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[3] Farkas, A., and Melville, H. W., Experimental Methods in Gas Reactions. Macmillan and Company, Ltd., London, 1939.

[4] Hougen, O. A., and Watson, K. M., Chemical Process Principles Charts. John Wiley and Sons, Inc., New York, 1947.

The values of y_o and y_n were determined from the simultaneous solutions of the equations,

$$x_o + x_n = 1 \quad , \tag{13}$$

$$y_o + y_n = 1 \quad , \tag{14}$$

$$y_o P_b = x_o P_o \quad \text{and} \tag{15}$$

$$y_n P_b = x_n P_n \quad . \tag{16}$$

Over the temperature range 76° to 90° K values of H_n, H_o and H_v were calculated using the appropriate equations presented above. The heat of vaporization for the mixture was calculated for a mean atmospheric pressure of 740 mm. Hg. Values of H_o, H_n and H_v at a pressure of 740 mm. Hg and various temperatures are presented in Table I in the Appendix.

Data from the measured heats of adsorption of nitrogen gas on the nickel-silica catalyst and the coconut charcoal described above are given in Table II in the Appendix.

Because the calorimeter used was an isothermal type, a small correction to the measured heat of adsorption, due to the isothermal heat of compression of the gas in the adsorption space, should be considered. Using the correction suggested by Beebe, Millard and Cynarski[5], it was found that this correction was very small, about one calorie per mole being the largest value obtained. It was therefore neglected.

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[5] Beebe, R. A., Millard, B., and Cynarski, J., "Heats of Adsorption of Nitrogen and Argon on Porous and on Non-Porous Carbon Adsorbents at -195°." J. Am. Chem. Soc. 75, 839-45 (1953).

2. Heats of Adsorption from Adsorption Isotherms

It is possible to calculate differential heats of adsorption from adsorption isosteres by means of the Clapeyron-Clausius equation. The form of the equation suggested by Hansen[6] for this purpose is

$$\left(\frac{d \ln p}{dt}\right)_V = \frac{H_d}{RT^2} \qquad (17)$$

where H_d is the differential heat of adsorption in cal./mole. A more convenient form of the equation which permits calculation from adsorption isotherms may be obtained by substituting dp/p for (d ln p), multiplying both sides of the resulting equation by dT and integrating along an isostere. The resulting equation is

$$\ln p = C - \frac{H_d}{RT} \quad , \qquad (18)$$

where C is a constant of integration and values of p and T must be evaluated at the same volume adsorbed. The value of H_d at each volume of adsorbed gas was obtained from three or more isotherms by the method of least squares. When only two isotherms were available, values of p and T from each isotherm at a given volume were substituted in equation 18 and the two resulting equations were added and solved for H_d. The resulting equation is

$$H_d = \frac{RT_1T_2}{T_2-T_1} \ln \frac{p_2}{p_1} \quad , \qquad (19)$$

where the subscripts 1 and 2 refer to the two different isotherms on which p and T were evaluated.

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6 Hansen, R. S., "Calculations of Heats of Adsorption from Adsorption Isosteres." J. Phys. Chem. 54, 411-15 (1950).

The equilibrium pressure and temperature corresponding to a given volume of gas adsorbed in the case of colloidal nickel were obtained from a smoothed plot of isotherms at several temperatures. When this was necessary, it was also necessary to eliminate, as much as possible, temperature variation throughout the entire isotherm. For this reason, the volume of gas admitted to the charcoal samples as described previously was adjusted so that the volumes of gas adsorbed on different isotherms were the same at the equilibrium pressures measured. Thus, the pressure at a given volume of adsorbed gas on each isotherm could be determined directly from the adsorption data without recourse to supplementary plots. In addition, it was unnecessary to keep the temperature constant throughout each series of adsorption measurements, provided that the temperature was accurately measured at the time the equilibrium pressure was measured.

The effect of thermal transpiration on heats of adsorption was not evaluated. Chessick, Healey and Zettlemoyer[7] found that transpiration corrections applied to their data for nitrogen adsorbed on molybdenum changed their final values by about three per cent at most. The temperatures employed in their adsorption studies differed by approximately 12° C; those of this study differed by about 4° C, hence a correction of only about one per cent would be expected in this work.

Values of the heats of adsorption calculated in this manner were compared with values at other temperatures and with other systems by dividing H_d by H_L, the heat of liquifaction of the adsorbed gas at the temperature of

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[7] Chessick, J. J., Healey, F. H., and Zettlemoyer, A. C., "Adsorption Studies on Metals. II. Absolute Entropies of Adsorbed Molecules on Molybdenum." J. Phys. Chem. 57, 912-15 (1953).

adsorption. The volume of adsorbed gas, V, was similarly compared by dividing it by V_m, the volume of gas required to form a monolayer of adsorbed gas molecules. The temperature at which H_L was determined was taken as the average temperature of the isotherms from which H_d was calculated. The data from which these calculations were made are given in Table III in the Appendix, and the results of these calculations are given in Table IV in the Appendix. Figure 5 presents these results along with others obtained calorimetrically under a previous contract[8]. The portion of this last curve below about five per cent coverage was believed to be in error and has been omitted in this report.

IV. DISCUSSION OF RESULTS

A. Apparatus and Procedures

1. Isothermal Calorimeter

It is believed that the calorimeter used for measuring heats of adsorption was satisfactory when relatively large amounts of heat were liberated in a short period of time. When small amounts of heat were liberated and especially when liberated over a long period of time, the results were not as accurate as desired.

Commercial oil-pumped tank nitrogen was used in this portion of the work without further purification. Although impurities make a great difference in the calculated heats of adsorption at low pressures due to preferential adsorption of certain elements, no such effect is expected when heats of adsorption are measured directly unless the heats of adsorption of the impurities are greatly different from that of the pure adsorbate. The main impurity in the nitrogen used was oxygen with inert gases making up most of the remainder of

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[8] DallaValle, J. M., Orr, C., Jr., and Blocker, H. G., op.cit.

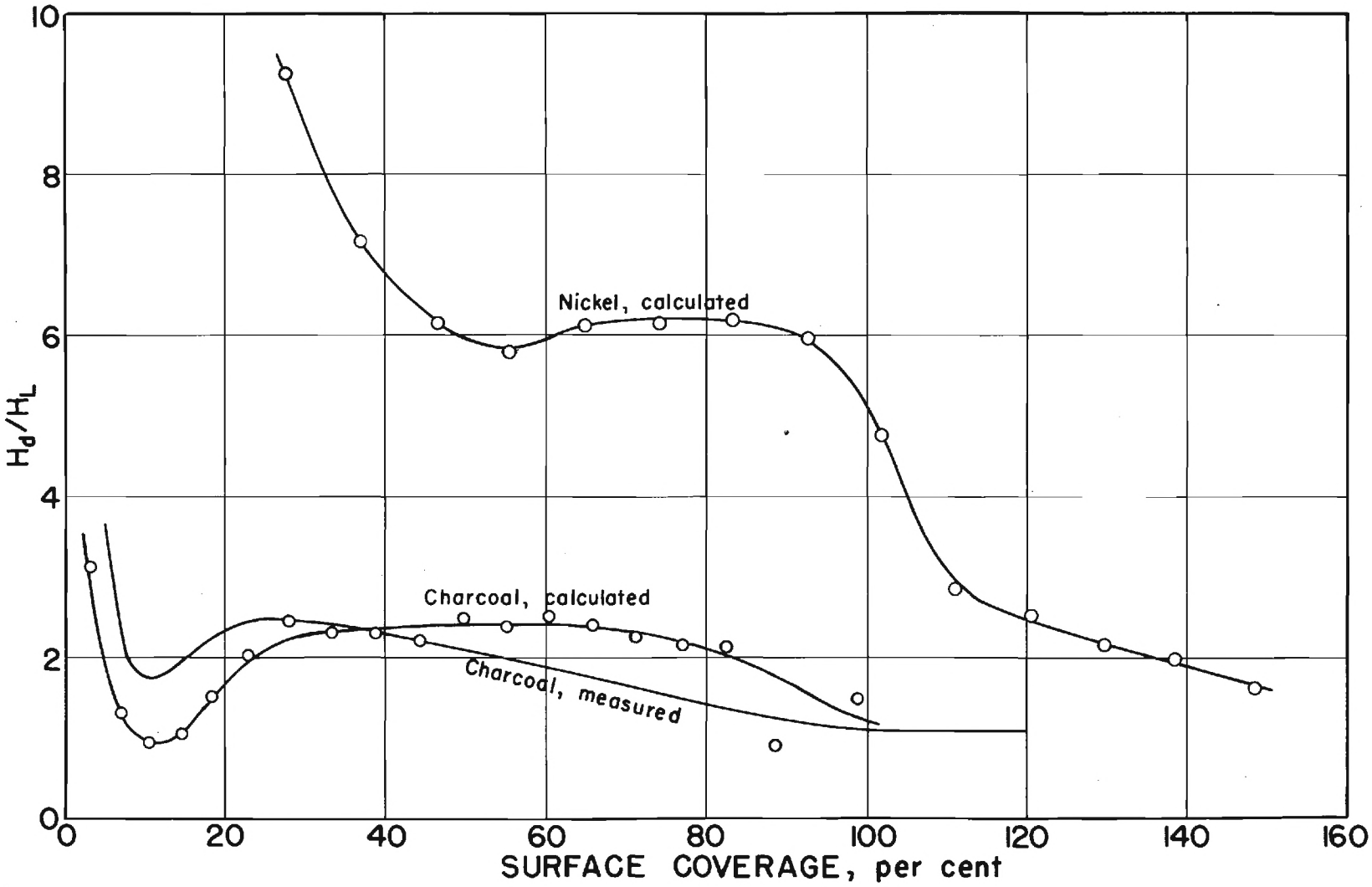

Figure 5. Heats of Adsorption of Nitrogen on Colloidal Nickel and Coconut Charcoal Calculated from the Clapeyron-Clausius Equation and Coconut Charcoal Measured in the Isothermal Calorimeter.

the impurities. Since the heat of adsorption of these impurities is of the same order of magnitude as that of nitrogen and, since they make up only a few tenths of one per cent of the adsorbent, it does not seem likely that large error could be caused by them. Experimental error due to other inaccuracies is greater than this amount; therefore,it is felt that the errors due to impurities in the gas are generally negligible in these measurements.

2. Isosteric System

The method of calculating heats of adsorption from adsorption isotherms was used in order that heats of adsorption of materials with small total-surface areas could be measured and so that an independent check on the results of the calorimeter might be obtained.

a. Induction Heater. The induction heater was used to heat the samples in order that a higher temperature for more thorough sample degassing might be obtained. This method was not used on the colloidal-nickel sample because it was feared that the metal would sinter if the temperature were raised too high; there was no such danger with charcoal. There was some indication that some of the charcoal was vaporized because a ring of dark deposit, presumably graphite, was formed in the sample tube just above the heated zone. For this reason, the heating time was kept as short as possible, usually two or three hours. The same sample was used on all of the measurements of charcoal reported here, yet the total deposit above the heated portion did not exceed a very thin film. For this reason it has been assumed that heating at 1,200° C caused no appreciable change in the charcoal surface. More complete degassing of the sample was obtained at the higher temperature in a short time than was obtained at the lower temperature previously employed, about 350° C, for 20 or more hours.

b. Pressure-Measurement Instruments. Accurate methods for measuring low equilibrium pressures are essential if reliable results at low coverage are to be obtained. This is especially true with a high-surface material such as charcoal, which at liquid-nitrogen temperature is almost two-thirds covered by adsorbed nitrogen molecules at an equilibrium pressure of only one mm. Hg.

Three devices employed to measure pressures have proven quite adequate in the ranges for which they were designed. Each of them functions best over a limited range of pressures, but the ranges overlap sufficiently for the devices to be checked against each other. These checks and other pressure measurements with the devices have been quite satisfactory.

The measurements on colloidal nickel were made before the cathetometer and ionization gauge were added to the apparatus. Low-pressure measurements were made with the McLeod gauge but sufficient data were not obtained in the low-pressure region to calculate heats of adsorption at very low surface coverages.

Most of the pressure measurements on charcoal were made with the McLeod gauge. The micrometer used with the cathetometer was especially useful in obtaining accurate measurements at pressures from 1 to 100 mm. Hg.

c. Gas-Purification System. A column packed with powdered copper was incorporated in the first design of this apparatus for the purpose of removing oxygen from the nitrogen gas to be adsorbed. Small quantities of other impurities in the nitrogen gas were found subsequently to cause large errors in the results. A comparison of the spectrum of the residual gases in the adsorption space with that of neon indicated that relatively large amounts of this gas were present and that helium was also present. Since a relatively large volume of nitrogen was adsorbed by charcoal during the determination of

the first few points of an isotherm while very little neon or helium was adsorbed, the concentration of inert gases in the sample space was increased tremendously. Although the inert gas present in the nitrogen was sufficient to invalidate equilibrium-pressure measurements in the low-pressure range, one calculation showed that less than 0.25 per cent inert gas was present in the increment of gas admitted to the sample. This emphasizes the importance of having as pure nitrogen as can be obtained for this type of measurement.

When the gas-purification system, as finally adapted, was employed, no indication of neon was found in the residual gases. Nevertheless, residual gas in the entire adsorption space, with the exception of the sample tube, was evacuated after each point before admitting a new increment of gas.

d. Temperature Regulation. The problem of temperature regulation was never completely eliminated. It was possible to regulate at the desired temperature to within approximately 0.1° C, however, by mixing liquid oxygen and nitrogen manually. No difficulty was encountered in measuring the temperature of the sample to within less than 0.1° C providing the temperature was not varying. An argon vapor pressure thermometer was used for this purpose.

B. Calculations and Results

1. Isothermal Calorimeter

As shown in Table I, the heat of vaporization of liquid-nitrogen and liquid-oxygen mixtures does not vary more than about two per cent in the temperature range in which all adsorption measurements were made. However, by using the values in Table I, errors in heat of adsorption measurements due to variations in the properties of the calorimetric medium were reduced to an insignificant figure.

As explained in a previous section of this report, calorimetric measurements were satisfactory unless the heat involved was relatively large and was evolved in a short time, e.g., less than one hour. Most of the measurements made with this system have been at low coverage, where equilibrium was approached slowly and where heat transfer from the sample was slow due to the low pressures attained in the sample tube. The data were found to be increasingly scattered as lower coverages were attempted. Above approximately three per cent coverage, the heat of adsorption has been reproduced to within about five per cent of the median values. As shown in Figure 5, approximate agreement between directly measured and calculated heats of adsorption were found in the case of charcoal.

2. Calculated Heats of Adsorption

Heats of adsorption for the colloidal nickel calculated from adsorption isotherms were obtained at surface coverages of from approximately 28 to 150 per cent. Lower coverage values were not obtained because the adsorption measurements on this material were made before all refinements in the adsorption apparatus were installed.

The differential heats of adsorption for nitrogen gas near the temperature of liquid nitrogen on nickel decreased to a minimum at about 1/2-surface coverage, increased again to a second maximum at about 3/4-surface coverage, decreased rapidly as single-layer coverage was approached and then seemed to approach the heat of vaporization asymptotically at more than single-layer coverage.

A similar pattern was followed in the case of the differential heats of adsorption for charcoal. Heats of adsorption for this material were obtained from approximately 3 to 95 per cent surface coverage. At the lower values of

surface coverage the heats of adsorption were relatively high and decreased to a minimum at about 1/6-surface coverage. The remainder of the curves for both charcoal and nickel were similar in shape over the range in which measurements were made on both materials. However, the values of the heats of adsorption at the maximum and minimum points were quite different, that for nickel being approximately three times as large as that for charcoal.

The values of the heats of adsorption for the charcoal were in approximately the same range as those measured by Beebe, Millard and Cynarski[9] for the adsorption of nitrogen on two different charcoals. The general shape of the differential heat of adsorption curves of the two charcoals measured by these investigators was similar to that obtained in this investigation except that the measurements reported herein indicated a minimum value of the heat at about 1/6-surface coverage which was not found by these other investigators.

C. Correlation of Results

Beebe and associates have attributed differences in heats of adsorption of charcoals to the fact that molecules adsorbed on the walls of fine pores may be attracted by more than one wall, resulting in increased heats of adsorption. Thus, a charcoal with small pores might be expected to give a larger heat of adsorption than one with large pores.

The charcoal used in this investigation has a specific surface area intermediate between that of the two charcoals used by Beebe and associates. The differential heats of adsorption from the charcoal used in this investigation were higher than that of either sample investigated by Beebe and associates for low coverages but rapidly decreased to a lower value than either of the other

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[9] Beebe, R. A., Millard, B., and Cynarski, J., op.cit.

charcoals exhibited. It then increased to a value about equal to that obtained by Beebe and coworkers for their higher-surface charcoal and then continued to follow approximately their curve.

The shape of differential heat of adsorption curves may be explained with the aid of the concepts of active sites and cooperative adsorption. The concept of active sites was first suggested by Taylor[10] and has proved very successful in explaining chemisorption, the action of poisons, etc. Cooperative adsorption, as the name implies, is the concept that adsorbate molecules influence each other during the adsorption process. Various investigators, among them T. L. Hill, H. M. Cassell and G. D. Halsey, as discussed by Emmett[11], have made use of this idea and suggested various theories related thereto.

A quantative theory of unequal active-site adsorption has recently been advanced by Bradshaw and Shuttleworth[12]. The experimental data reported herein and that of other investigations may be explained by it, although such explanation does not, at this stage, prove the theory correct. This theory proposes that the differential heat of adsorption of a gas on a solid surface is the sum of the heat of adhesion of the gas to the solid and a determinable fraction of the heat of condensation of the gas. The number of nearest-neighbor atoms in the solid determines the activity of a given adsorption site. The contribution of the heat of condensation is determined from the number of nearest-neighbor adsorbed-gas molecules and the number of nearest-neighbor gas molecules in the condensed or solid state.

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[10] Taylor, H. S., "A Theory of the Catalytic Surface." Proc. Roy. Soc. A 108, 105-11 (1925).

[11] Emmett, P. H., (Editor), Catalysis, Part I. Reinhold Publishing Corporation, New York, 1954.

[12] Bradshaw, B. C., and Shuttleworth, Rose A., Signal Corps Engineering Laboratories, Fort Monmouth, N. J. Unpublished work.

This theory may be expressed quantitatively by the equation

$$H_d = N_s H_s + \frac{N_a}{N_c} H_c \ , \qquad (20)$$

where N_s = number of nearest-neighbor atoms of the solid to which the adsorbed-gas molecule is directly attached,

N_a = number of effective nearest-neighbor adsorbed-gas molecules,

N_c = number of effective nearest-neighbor adsorbent molecules in the condensed or solid state,

H_s = energy of attachment of a gas molecule to each solid atom and

H_c = heat of condensation or vaporization.

The number of solid atoms to which each adsorbed molecule is attached may vary from one to several with the energy of attachment of the gas molecule increasing in direct proportion to the number of solid atoms involved. It has been shown that most of the adsorption sites involve only one solid atom. Some of the remaining sites involve two solid atoms and only a relatively few sites involve three or more atoms. The number of sites involving four or five atoms is very small. As the adsorption of a gas progresses to the completion of a monolayer, the most active sites, i.e., those involving most solid atoms, are occupied first and other sites are then occupied in the order of decreasing activity.

The results for the adsorption of nitrogen by charcoal obtained in this investigation may be easily explained using this theory. At the beginning of the adsorption measurements, the most active sites are being occupied and the heat of adsorption is high. As the volume of gas adsorbed increases, the less active sites are occupied and the heat of adsorption decreases to a minimum. Prior to this time the effect of other adsorbed gas molecules is negligible;

the distance between adsorbed molecules being too great for any later effects. The second term in equation 20 is negligible, in other words. When more gas is adsorbed, the effect of adjacent molecules becomes increasingly important, and the heat of adsorption increases to a maximum and then decreases as the adsorbed monolayer nears completion. After the monolayer of adsorbed gas is completed, the effect of the atoms of the solid on the gas molecules adsorbing on the second layer becomes small, i.e., the ratio N_a/N_c approaches unity and the heat of adsorption approaches the heat of condensation. The lowest points at about 10 per cent coverage, as shown in Figure 5, are felt to be low, however there is no experimental evidence at the present that they are.

As has been noted previously, the differential heat of adsorption of the colloidal nickel was approximately three times that of the charcoal. A minimum-energy point for the nickel also occurred at approximately three times the per cent surface coverage of that for the corresponding charcoal minimum. Both of these facts indicate that a greater proportion of the more active sites are present on the nickel surface than on the charcoal surface. For this reason it might be expected that the nickel would be a better catalyst than charcoal. This, of course, is well-known.

From the foregoing discussions the importance of heat of adsorption measurements in studies of the mechanisms of adsorption and catalysis should be apparent. This is especially true at low coverage, where the influence of the more active sites can be studied.

V. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions may be drawn from, or are substantiated by, the results of this investigation:

(1) Better heat of adsorption data at low-surface coverage were obtained by calculation from adsorption isotherms using the Clapeyron-Clausius equation than were obtained by actual measurement, although results from the two types of measurements indicated general agreement.

(2) Gases of highest purity must be used in obtaining meaningful heat of adsorption data.

(3) The heat evolved by adsorbing-gas molecules depends upon the possibility of interaction with atoms in the adsorbent surface as well as interaction with other adsorbed-gas molecules.

(4) Differential heat of adsorption information can reveal much information about the surface structure of adsorbents and catalysts.

Further studies of heat of adsorption, particularly adsorption at low-surface coverage, are strongly recommended. From such studies very valuable information on the properties of surfaces will result.

VI. PERSONNEL

The technical personnel who worked on this project and the percentage of working time each devoted to the project are shown below:

Name	Title	Per Cent of Working Time Devoted to Project
J. M. DallaValle	Project Director (Prior to Oct. 15, 1953)	12
Clyde Orr, Jr.	Project Director (After Oct. 15, 1953) Research Engineer (Prior to Oct. 15, 1953)	44
H. G. Blocker	Research Engineer	95
Jane B. Garrett	Research Assistant	26
M. T. Gordon	Research Engineer	5
R. A. Young	Research Physicist	1/2
W. E. Wolf	Research Physicist	1

Dr. DallaValle was the Project Director of this investigation from its beginning until October 15, 1953, at which time he was granted leave of absence from Georgia Tech to serve as a Fulbright professor in Milan, Italy. Dr. Orr was then appointed project director. Mr. Gordon, a chemical engineer with considerable experience in electronics, helped set up the ionization gauge and induction heater, but did not participate directly in the research on heats of adsorption. Mr. Young and Mr. Wolf, x-ray specialists, made a short study of the crystal structure of the colloidal nickel by x-ray line-broadening methods.

Respectfully submitted:

Clyde Orr, Jr.

Clyde Orr, Jr.,
Project Director

H. G. Blocker

H. G. Blocker,
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Jane B. Garrett,
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VII. APPENDIX

TABLE I

CALCULATED VALUES OF HEAT OF VAPORIZATION
OF NITROGEN, OXYGEN AND NITROGEN-OXYGEN MIXTURES

Temp. (°K)	Heat of Vaporization of Nitrogen, H_n (cal./mole)	Heat of Vaporization of Oxygen, H_o (cal./mole)	Heat of Vaporization of Nitrogen-Oxygen Mixture at 740 mm. Hg, H_v (cal./mole)
76	1,346	1,788	1,346
78	1,330	1,770	1,343
80	1,312	1,752	1,362
82	1,295	1,733	1,391
84	1,276	1,712	1,432
86	1,257	1,689	1,487
88	1,233	1,661	1,555
90	1,210	1,632	1,632

TABLE II

EXPERIMENTAL NITROGEN HEAT OF ADSORPTION DATA

1. Nickel-Silica Catalyst G-12 evacuated 96 hrs. at 350° C to 0.1 μ.

p (mm.Hg)	V (cc./g.)	T_s (°K)	H_d (cal./mole)
0.0	0.43	79.4	3,050
0.0	1.36	79.4	3,190
0.4	2.86	79.4	2,580
0.7	4.43	79.4	2,410
1.0	6.64	79.4	2,350
1.5	9.50	77.9	1,790
1.8	12.30	77.9	2,800
2.1	15.55	77.9	2,800
3.0	18.96	77.9	2,860

2. Coconut Charcoal evacuated 200 hrs. at 500° C to 0.01 μ.

p (mm.Hg)	V (cc./g.)	T_s (°K)	H_d (cal./mole)
0.0	0.35	77.8	5,210
0.0	0.73	77.8	3,450

3. Coconut Charcoal evacuated 24 hrs. at 500° C to 0.07 μ.

p (mm.Hg)	V (cc./g.)	T_s (°K)	H_d (cal./mole)
0.0	0.61	78.6	2,690
0.0	1.35	78.6	2,100
0.0	2.31	78.9	---
0.0	3.38	78.9	4,290
0.0	4.39	78.7	---
0.0	5.23	78.7	4,030
0.0	6.15	78.7	4,090
0.0	7.66	78.5	---
0.0	9.23	78.5	4,480
0.0	11.01	78.5	4,570
0.0	12.92	78.5	4,590
0.0	14.88	78.1	5,350
	16.59	78.1	4,570
0.0	18.40	78.1	4,650

4. Coconut Charcoal evacuated 24 hrs. at 450° C to 0.05 μ.

p (mm.Hg)	V (cc./g.)	T_s (°K)	H_d (cal./mole)
0.0	0.27	78.5	---
0.0	0.51	78.5	4,620
0.0	0.86	78.8	3,600
0.0	1.30	78.8	2,990
0.0	1.73	78.8	6,330
0.0	2.35	78.9	4,620
0.0	3.00	79.2	4,260
0.0	3.58	79.2	4,340
0.0	4.23	79.2	3,640
0.0	4.81	79.2	4,340
0.0	5.88	79.2	3,950
0.0	7.76	79.3	2,550
0.0	9.79	79.3	2,240

5. Coconut Charcoal evacuated 48 hrs. at 400° C to 0.01 μ.

p (mm.Hg)	V (cc./g.)	T_s (°K)	H_d (cal./mole)
0.0	0.46	77.9	5,300
0.0	0.97	77.9	5,170
0.0	1.53	77.9	5,670
0.0	2.35	77.9	4,620
0.0	3.22	77.9	4,720
0.0	4.28	77.9	5,080
0.0	5.14	78.0	5,740
0.0	6.14	78.0	6,130
0.0	7.12	78.0	4,670
0.0	8.10	78.0	5,240
0.0	9.14	78.0	4,650
0.0	10.10	78.0	4,820
0.0	11.07	78.0	4,660
0.0	12.10	78.1	5,600
0.0	13.08	78.1	5,020
0.0	14.14	78.1	5,420
0.0	15.61	78.1	4,790
0.0	17.06	78.1	4,860
0.0	18.46	78.1	---
0.0	19.83	78.1	4,810
0.0	21.24	78.1	5,210
0.0	22.46	78.1	4,130
0.0	24.15	78.1	4,400
0.0	25.37	78.1	4,420

TABLE III

EXPERIMENTAL NITROGEN-GAS ADSORPTION DATA

1. Colloidal-Nickel Powder evacuated 18 hrs. at 300° C to 0.01 μ.

p (mm. Hg)	V (cc./g.)	T_s (°K)
0.042	1.19	77.9
2.7	3.04	77.9
6.0	3.81	77.9
13.9	4.70	77.9
31.2	5.55	77.9
63.4	6.09	77.9
97.5	6.70	77.9
134.1	7.22	77.9
171.5	7.76	77.9
208.2	8.35	77.9
243.2	8.57	77.9

2. Colloidal-Nickel Powder evacuated 200 hrs. at 250° C to 0.1 μ.

p (mm. Hg)	V (cc./g.)	T_s (°K)
0.0076	0.60	80.0
0.050	1.30	80.0
0.349	2.05	80.0
1.65	2.77	80.0
4.0	3.20	80.0
7.1	3.74	80.0
14.5	4.31	80.0
28.1	4.82	80.0
44.2	5.26	80.0
63.8	5.55	80.0
84.7	5.79	80.0

3. Colloidal-Nickel Powder evacuated 18 hrs. at 300° C to 0.01 μ.

p (mm. Hg)	V (cc./g.)	T_s (°K)
0.40	1.82	80.0
6.1	3.63	80.0
12.7	4.42	80.0
25.6	5.13	80.0
48.0	5.77	80.0
76.9	6.30	80.0
112.6	6.82	80.0
154.1	7.46	80.0
197.2	8.13	80.0

4. Colloidal-Nickel Powder evacuated 16 hrs. at 300° C to 0.01 μ.

p (mm. Hg)	V (cc./g.)	T_s (°K)
19.0	3.73	80.8
50.8	4.49	80.8
96.0	5.06	80.8
151.0	5.57	80.8
212.8	6.05	80.8
272.4	6.56	80.8
330.7	7.09	80.8
389.6	7.61	80.8
458.0	8.42	80.8

(Continued)

TABLE III (Continued)

EXPERIMENTAL NITROGEN-GAS ADSORPTION DATA

5. Colloidal-Nickel Powder evacuated 20 hrs. at 300° C to 0.01 μ.

p (mm. Hg)	V (cc./g.)	T_s (°K)
0.0105	0.41	83.0
0.026	0.98	83.0
2.2	1.27	83.0
5.2	1.64	83.0
11.5	2.10	83.0
23.0	2.57	83.0
39.1	2.93	83.0
61.5	3.25	83.0
88.5	3.50	83.0
116.0	3.78	83.0
147.9	3.90	83.0
178.9	4.15	83.0
218.0	4.39	83.0
261.9	4.58	83.0
312.5	4.86	83.0
373.5	5.26	83.0

6. Colloidal-Nickel Powder evacuated 20 hrs. at 300° C to 0.001 μ.

p (mm. Hg)	V (cc./g.)	T_s (°K)
0.0020	0.50	78.0
0.0110	1.00	78.0
0.040	1.71	78.0
0.370	2.30	78.0
1.38	2.86	78.0
3.0	3.34	78.0
4.9	3.75	78.0
8.3	4.28	78.0
14.1	4.73	78.0
25.0	5.18	78.0
38.2	5.52	78.0
58.1	5.88	78.0
81.1	6.22	78.0
109.7	6.62	78.0
141.6	7.07	78.0
175.3	7.52	78.0

7. Colloidal-Nickel Powder evacuated 18 hrs. at 300° C to 0.01 μ.

p (mm. Hg)	V (cc./g.)	T_s (°K)
0.040	0.64	82.0
0.735	1.33	82.0
3.0	1.84	82.0
7.9	2.30	82.0
13.1	2.72	82.0
23.9	3.07	82.0
34.9	3.33	82.0
49.9	3.56	82.0
67.0	3.79	82.0
88.0	3.96	82.0
114.0	4.16	82.0
139.0	4.31	82.0
169.3	4.52	82.0
203.1	4.80	82.0
245.0	5.02	82.0

8. Coconut Charcoal evacuated 2 hrs. at 1,200° C to 3 μ.

p (mm. Hg)	V (cc./g.)	T_s (°K)
0.820	187.5	82.9
2.00	205.3	82.5
5.75	222.4	82.5
13.62	240.8	82.5
32.26	259.5	82.5
62.40	279.7	82.0
119.6	298.4	82.0
88.66	300.8	78.7
193.8	314.7	78.7
386.6	314.9	81.8
315.5	320.5	79.0
520.3	321.9	82.5

(Continued)

TABLE III (Continued)

EXPERIMENTAL NITROGEN-GAS ADSORPTION DATA

9. Coconut Charcoal evacuated 3 hrs. at 1,200° C to 1 μ.

p (microns)	V (cc./g.)	T_s (°K)
0.01	10.8	77.9
0.15	23.4	78.0
0.39	36.3	78.0
0.75	49.4	78.0
1.90	62.9	78.0
3.5	78.0	78.0
7.6	95.1	78.0

10. Coconut Charcoal evacuated 2 hrs. at 1,200° C to 1.5 μ.

p (microns)	V (cc./g.)	T_s (°K)
0.02	10.9	80.0
0.20	23.4	80.1
0.55	36.3	80.3
1.0	49.4	80.2
2.5	62.8	79.8
5.5	78.0	80.1
13.0	95.2	80.1

11. Coconut Charcoal evacuated 2 hrs. at 1,200° C to 2 μ.

p (microns)	V (cc./g.)	T_s (°K)
0.27	23.4	82.5
0.60	36.3	82.5
1.2	49.4	82.5
3.8	63.0	82.5

12. Coconut Charcoal evacuated 2 hrs. at 1,200° C to 4 μ.

p (microns)	V (cc./g.)	T_s (°K)
7.9	95.1	78.1
16.5	113.0	78.4
27	131.5	77.8
52	150.0	77.9
110	168.8	77.8
242	187.0	77.8
613	205.3	77.8
1,800	223.5	77.8
4,620	241.6	77.8
11,420	260.2	77.8
24,400	278.6	77.8

13. Coconut Charcoal evacuated 2 hrs. at 1,200° C to 3 μ.

p (microns)	V (cc./g.)	T_s (°K)
9.5	78.0	82.5
20.0	95.1	82.5

14. Coconut Charcoal evacuated 2 hrs. at 1,200° C to 4 μ.

p (microns)	V (cc./g.)	T_s (°K)
0.01	10.9	78.0
0.08	23.4	78.3
0.31	36.3	78.6
0.70	49.4	78.3
1.60	62.9	78.3
3.6	78.0	78.3

15. Coconut Charcoal evacuated 3 hrs. at 1,200° C to 3 μ.

p (microns)	V (cc./g.)	T_s (°K)
42	113.1	82.5
80	131.7	82.5
146	150.1	82.5
360	168.9	82.5
760	187.6	82.5

TABLE IV

CALCULATED HEATS OF ADSORPTION OF NITROGEN

Adsorbent	T_s (°K)	Surface Coverage (Per Cent)	H_d/H_L
Colloidal-Nickel Powder	80.7	27.8	9.23
Colloidal-Nickel Powder	80.2	37.1	7.16
Colloidal-Nickel Powder	80.2	46.4	6.18
Colloidal-Nickel Powder	80.3	55.7	5.79
Colloidal-Nickel Powder	80.2	64.9	6.12
Colloidal-Nickel Powder	80.2	74.2	6.17
Colloidal-Nickel Powder	80.2	83.5	6.20
Colloidal-Nickel Powder	80.2	92.8	5.98
Colloidal-Nickel Powder	80.0	102.0	4.77
Colloidal-Nickel Powder	79.3	111.3	2.85
Colloidal-Nickel Powder	79.2	120.6	2.52
Colloidal-Nickel Powder	79.2	129.9	2.19
Colloidal-Nickel Powder	79.2	139.1	1.99
Colloidal-Nickel Powder	79.2	148.4	1.80
Coconut Charcoal	79.0	3.2	3.13
Coconut Charcoal	80.2	6.9	1.28
Coconut Charcoal	80.3	10.7	0.95
Coconut Charcoal	80.3	14.6	1.02
Coconut Charcoal	80.1	18.5	1.51
Coconut Charcoal	79.0	23.1	2.04
Coconut Charcoal	79.0	28.1	2.42
Coconut Charcoal	80.4	33.5	2.24
Coconut Charcoal	80.1	38.9	2.25
Coconut Charcoal	80.2	44.4	2.19
Coconut Charcoal	80.1	49.9	2.45
Coconut Charcoal	80.1	55.4	2.37
Coconut Charcoal	80.1	60.7	2.45
Coconut Charcoal	80.1	66.0	2.41
Coconut Charcoal	80.1	71.4	2.26
Coconut Charcoal	80.1	76.9	2.15
Coconut Charcoal	79.9	82.6	2.15
Coconut Charcoal	80.3	88.7	0.88
Coconut Charcoal	80.7	95.3	1.42